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**THE EFFECTS OF HIGHWAY ENVIRONMENTAL CONDITIONS ON
PHOTOCATALYTIC PAVEMENT'S ABILITY TO REDUCE NITROGEN OXIDES**

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Master of Science

in

The Interdepartmental Program in Engineering Science

by
Heather Dylla
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ABSTRACT

Nitrogen oxides (NO_x) emitted from vehicle exhaust are associated with negative health impacts and are a precursor to ozone. Self-cleaning, air-purifying concrete pavement is a rapidly emerging technology that can degrade pollutants such as NO_x through heterogeneous photocatalysis. Although this technology has the potential to support environmentally friendly road infrastructure, a number of design and operational parameters may affect its effectiveness and thus need to be evaluated. The goal of this study was to measure the NO_x reduction efficiencies from photocatalytic pavements under various environmental conditions common to highways. To achieve this goal, the objectives were to: (a) evaluate the influence of photocatalytic layer design and operating parameters on the efficiency of photocatalytic concrete pavement; (b) measure the impact of mixed pollutants on NO_x reduction efficiency; and (c) measure the impact of roadway contaminants on NO_x reduction.

To achieve the first objective, the effects of relative humidity level, pollutants' flow rate, and photocatalytic layer design parameters, including titanium dioxide (TiO_2) percent content and aggregate sizes, were investigated. The environmental efficiency of the samples to remove NO_x from the atmosphere was measured using a newly developed laboratory setup. The photocatalytic layer designs without fines achieved the highest photodegradation rates. In addition, the increase from 3% to 5% TiO_2 resulted in minimal improvement to the NO_x removal efficiency. To achieve the second objective, NO_x reduction efficiencies were measured for various NO_2/NO_x ratios at various flow rates and humidity levels. Increasing the flow rate and NO_2/NO_x ratio negatively affects the effectiveness of the photocatalytic process. The highest

photodegradation rate was observed at 25% relative humidity, which balances the availability of hydroxyl radicals at the surface with NO_x contact with the photocatalytic surface. To achieve the third objective, three common roadway contaminants were tested - dirt, de-icing salt, and motor oil - at two contrasting coverage levels. The contaminants had a strong, negative impact on the photocatalytic NO_x removal efficiency. The impact of contaminants' coverage was largely dependent on the soilure type, with oil having the largest negative impact. An increase in the flow rate and air relative humidity also resulted in lower NO_x efficiencies.

CHAPTER 1

INTRODUCTION

In recent years, environmental concerns of pollution and resource depletion represent major concerns for society. Air quality in the vicinity of large cities was linked with serious health hazards. Many of these health hazards are associated with nitrogen oxides (NO_x) and volatile organic compounds (VOCs) in the air, which in turn are caused by high traffic volumes and combustors. These pollutants may also travel long distances to produce secondary pollutants, such as acid rain or ozone (Beeldens 2006).

Highway operations have major environmental impacts during construction and service (EPA 1994). Road microenvironments contribute to 29% of the VOCs, 35% of the NO_x, and 58% of the carbon monoxide (CO) emitted in the US (Kuhns et al. 2004). These concentrations are often higher in cities where urban development and increased traffic volumes add to emissions, while street canyon conditions inhibit dispersion, resulting in high ground level concentrations. These high concentrations often surpass the concentrations of industrial sources, making traffic emissions the primary source of urban air pollution (Baldauf et al. 2008; Thoma et al. 2008; Chen et al. 2008; Berkowicz et al. 2006). Consequently, many adverse health effects are being linked to areas of within 100 meters from roads, where pollution is not fully diluted (Thoma et al. 2008). This area contains more than 35 million Americans, thus making transportation pollution a major concern (Thoma et al. 2008).

A series of studies were initiated from the Environmental Protection Agency (EPA) to investigate and mitigate traffic emissions (Thoma et al. 2008). Currently, researchers are investigating the dispersion characteristics of various pollutants, in order to identify the impacting factors (Thoma et al. 2008). However, these studies focus on the variables influencing pollution in order to modify traffic and city planning operations and motor vehicle inspection,

rather than reducing air pollutant concentrations, once these concentrations reach the atmosphere. Improvements to vehicle operations such as the 1990's introduction of the catalytic converter, which reduces NO_x emissions, are another possible solution (Berkowicz et al. 2006). However, it may take years for the majority of vehicle users to adopt any of the new technologies to make an overall impact on the environment. Therefore, a solution is needed to remove pollutants once emitted to the atmosphere.

One potential solution to pollution remediation may be heterogeneous photocatalysis, in which the natural decomposition process is accelerated. Photocatalytic compounds such as titanium dioxide (TiO₂) can trap and absorb organic and inorganic particles in the air, removing harmful air pollutants such as NO_x and VOCs in the presence of UV light (sunlight) (Beeldens 2008). In addition, the super-hydrophilic or super-hydrophobic properties allow self-cleaning in the presence of rain (Fujishima and Zhang 2006, Benedix et al. 2000). Photocatalytic compounds may be utilized to construct air purifying concrete pavement by integrating titanium dioxide particles within a thin, concrete surface layer. The properties of these particles to self-clean and to decompose pollutants are maintained and even enhanced when used with concrete. Further, the large surface area of concrete pavements, in close proximity to pollutants in urban areas, makes it an ideal substrate for heterogeneous photocatalysis air remediation (Beeldens 2008).

1.1 Problem Statement

Recent literature has shown that photocatalytic compounds can significantly reduce NO_x. The use of photocatalytic compounds in pavement, in close proximity to the source of pollutants, is a promising technology. However, the application of this technology to pavements is still in its infancy, and many environmental, design, and operational factors still need to be evaluated.

Furthermore, many factors have not been investigated such as the effects of mixed NO and NO₂ concentrations and the effects of pavement soilures including dirt, motor oil, and deicing salts on NO_x removal efficiency.

1.2 Objectives

To address the aforementioned problem statement, the objectives of this study were to: (a) evaluate the influence of photocatalytic layer design under various operating parameters on the efficiency of photocatalytic concrete pavement; (b) measure the impact of mixed NO₂ and NO concentrations on NO_x reduction efficiency; and (c) measure the impact of roadway contaminants, including dirt, motor oil and deicing salts on NO_x reduction. Results of this project propose a design for a titanium dioxide photocatalytic concrete surface coating. The environmental benefits from the proposed coating were evaluated under common environmental conditions of highways to further understand the potential of photocatalytic pavements to reduce harmful air pollution.

1.3 Research Approach

To achieve the objectives of this study, the research methodology proposed consisted of eight tasks split over three project phases.

Phase 1: Develop a photocatalytic concrete surface layer for air purification

Task 1: Prepare experimental samples

Task 2: Create an experimental setup for photocatalytic testing

Task 3: Measure photocatalytic efficiency under known environmental variables

Task 4: Test durability of photocatalytic layer against cracking

Phase 2: Evaluate the environmental effectiveness of photocatalytic concrete surface layers in photodegrading mixed NO₂ and NO gases

Task 5: Measure impact of mixed NO₂ and NO gas on photocatalytic efficiency

Task 6: Identify any interaction impacts due to known environmental variables

Phase 3: Evaluate the environmental effectiveness of photocatalytic concrete surface layers in photodegrading NO_x, exposed to common roadway contaminants

Task 7: Measure impact of roadway contaminants on photocatalytic efficiency

Task 8: Identify any interaction impacts due to known environmental variables

The first phase of the project was to develop a photocatalytic concrete surface layer for air purification. Concrete samples were prepared using a two lift concrete system with two aggregate size distributions and two percentages of TiO₂ contents. A new laboratory setup was designed to measure the photocatalytic reductions of NO_x in pavements. Using this setup, the NO_x reduction of each mix was measured under known environmental parameters, including three levels of humidity and three levels of air flow. Each photocatalytic layer design was tested under the Hamburg loaded wheel tester to ensure layer durability, due to cracking from repeated traffic loading. Trends of environmental and photocatalytic layer parameters that affect the effectiveness of the TiO₂ coating's environmental performance were developed. The outcome of this phase identified an optimal photocatalytic layer design, thus achieving objective (a).

The second phase was to evaluate the environmental effectiveness of TiO₂ photocatalytic pavements in photodegrading mixed NO₂ and NO gases from the atmosphere. The same four samples created in Phase one, were used in Phase two to verify the optimal photocatalytic layer design previously identified. In addition, the known environmental factors of humidity level and flow rate were also tested under various NO₂/NO_x ratios, to identify any variable interactions. A

partial factorial design was conducted for NO₂/NO_x, flow rate, aggregate structure, and TiO₂ content, to provide an indication of the influence of each factor on the photocatalytic effectiveness. Further investigation was conducted on the significant variables identified, including the relative humidity, flow, and NO₂/NO_x ratios to develop the associated trends, thus achieving objective (b).

The third and final phase was to evaluate the environmental effectiveness of photocatalytic concrete surface layers in photodegrading NO_x, when exposed to common roadway contaminants. Three common roadway contaminants were chosen - dirt, de-icing salt, and motor oil - each of which tested at two soilure coverage levels. A control run was also conducted, which was tested without any soiling, for comparison. The optimum photocatalytic layer design determined from the previous two phases was provided by the utilized photocatalytic pavement samples. Main effects of the relative humidity, contaminant coverage level, and flow rate were calculated for two levels for each factor; potential interactions between variables were identified. Further analysis was conducted on the significant variables identified inclusive of contaminant, relative humidity, and flow to develop the associated trends, thus achieving objective (c).

Results of each project phase are discussed in separate chapters: Phase 1-Chapter 3, Phase 2-Chapter 4, and Phase 3-Chapter 5. The last chapter consolidates the project results and also includes future recommendations and research ideas.

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CHAPTER 2

LITERATURE REVIEW

2.1 Environmental Photocatalysis Historical Overview

Initial interest in environmental photocatalysis began in the 1970s, initiated by Fujishima and Honda's research in photoelectrochemical solar energy conversion. Through biomimicry of plant photosynthesis, the researchers attempted to replicate the photo-induced redox reactions, by oxidizing water and reducing carbon dioxide, using a semiconductor irradiated by UV light (Fujishima and Zhang 2006). To accomplish this, the semiconductor is used as an electrode, which is connected to a counter electrode to generate electrical work while driving the redox chemical reactions (Fujishima and Honda 1972). TiO_2 was the semiconductor chosen, due to a positive valence band edge that theoretically can oxidize water to oxygen (Fujishima et al. 2000). Fujishima and Honda found that when the surface was irradiated, a current was created such that oxidation occurred at the TiO_2 electrode and reduction at the counter electrode (Fujishima and Honda 1972). This proved that water could be decomposed into oxygen and hydrogen from solar irradiation, preferred since solar energy equates to roughly 5×10^{24} J per year (Cassar 2004).

The photoelectrochemistry concepts described were extended to research in heterogeneous photocatalysis applications by removing the external circuit (Fujishima and Zhang 2006). In 1977, Frank and Bard were one of the first to demonstrate this, by illustrating the decomposition of cyanide in water. Since then, increased interest in environmental photocatalysis was realized which caused TiO_2 to be applied to glass, tile, paper, and pavements for self-cleaning materials, water purification, air purification, sterilization, and oil spill remediation. From these studies, it has been shown that organic and inorganic compounds can be completely decomposed and that the TiO_2 surface has the ability to self-regenerate (Fujishima

and Zhang 2006). Therefore, rather than an absorption of pollutants that is common to traditional air purification methods, heterogeneous photocatalysis can decompose pollutants to nonhazardous waste products with little energy requirements (Zhao and Yang 2003).

2.2 Heterogeneous Photocatalysis Mechanism

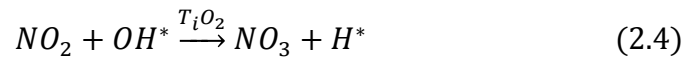
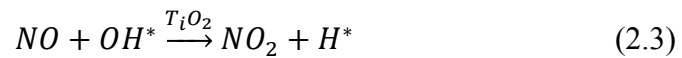
Heterogeneous photocatalysis requires a semiconductor photocatalyst in contact with a liquid or gas reaction medium. There are many semiconductors available for heterogeneous photocatalysis, such as CdS, ZnS, SnO₂, WO₃, SiO₂, ZrO₂, ZnO, Nb₂O₃, Fe₂O₃, SrTiO₃, and TiO₂ (Fujishima et al. 2000, Li et al. 2001, Zhao and Yang 2003). The photocatalytic ability of each is determined by the respective band gap, whereas the photocatalytic efficiency is impacted by crystal type, particle size, and any crystal modifications (Zhao and Yang 2003).

TiO₂, the first type of semiconductor material studied due to its positive valence band edge that oxidizes water to oxygen, remains the most popular today (Fujishima et al. 2000). Titanium dioxide has three crystal arrangements: anatase, rutile, and brookite (Husken et al. 2009). Of the three, anatase exhibits the highest photoactive efficiencies (Zhao and Yang 2003). Its excellent photocatalytic properties, such as highly oxidizing, photogenerated holes that produce hydroxyl radicals, as well as photogenerated electrons that produce superoxides from dioxygen, play an important role in photocatalytic reactions (Fujishima et al. 2000). Additional characteristics of TiO₂ that make it an ideal for heterogeneous photocatalytic applications are its near transparency (especially useful in windows and glass), high stability in presence of aqueous electrolyte solutions, superhydrophilicity, relative cheapness, and commercial availability (Cassar 2004, Fujishima and Zhang 2006, Diamanti et al. 2008, Toma et al. 2009).

When TiO_2 is exposed to energy, from photons, that exceeds the band gap energy of 3.2 eV, an electron is expelled from the valence band to the conduction band, leaving a hole behind (Figure 2.1) (Zhao and Yang 2003, Fujishima et al. 2000). For TiO_2 , this process is initiated by energy from a UV light wavelength determined by the electromagnetic radiation, $h\nu$, where h is Planck's constant and ν is the frequency of light. The production of electron-hole pairs, called excitons, results in redox or oxidation chemical reactions (Fujishima et al. 2000, Zhao and Yang 2003, Hunger et al. 2008). In the presence of water, these oxidizing holes, h^+ , and photogenerated electrons, e^- , create hydroxyl radicals and superoxides respectively, shown in Equations 2.1 and 2.2 (Fujishima et al. 2000).



The resulting hydroxyl radicals and superoxides are key for oxidation or reduction reactions allowing for degradation of pollutants in the oxidation of NO_x to water soluble nitrates, as shown in Equations 2.3 and 2.4 below (Beeldens 2008):



This complete process is illustrated in Figure 2.1 on the following page.

2.3 Photocatalysis Pavements

Titanium dioxide mediates heterogeneous photocatalysis, and therefore can be a self-cleaning material, possibly useful in environmental pollution remediation (Fujishima and Zhang 2006). For air purification, large surface areas in close contact to high pollution concentrations are ideal

(Beeldens 2006). For this purpose, applications of TiO_2 were expanded to create photocatalytic pavements.

The versatility, relatively low cost, and large-scale application possibilities of cement/concrete make it an important and popular substrate (Lackhoff et al 2003). In addition, some research shows synergetic effects have been exhibited when TiO_2 has been used with cementitious and various construction materials (Cassar 2004). As a result, concrete represents the primary pavement material investigated.

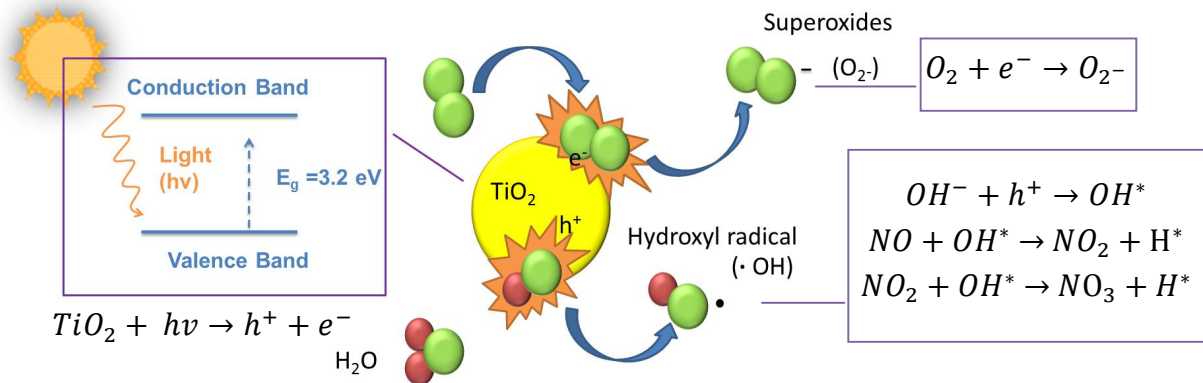


Figure 2.1 Photocatalytic Process (modified from Nano 2000)

2.3.1 Developments in Concrete Substrates

TiO_2 was first introduced to cement materials used in buildings to retain the white color and aesthetic characteristics, thus creating a self-cleaning effect (Husken et al. 2009, Cassar et al. 2003). The discoloration, particularly on white concrete, is due to the accumulation of organic compounds. Initial studies of photocatalytic concretes were based on colorimetric tests. Exposing the surface with an organic dye such as rhodamine B, the colorimetric measurements monitored the reduction of pollution on the surface when exposed to UV irradiation (Cassar 2004).

Current research switches the focus from self-cleaning concrete to an evaluation of TiO_2 for air remediation techniques. Many chemicals have shown an ability to degrade from TiO_2

photocatalytic activity with concrete substrates, such as NO_x, SO_x, NH₃, CO, as well as volatile organic carbons, such as benzene, and toluene, organic chlorides, aldehydes, and polycondensated aromatics (Cassar 2005). A concrete matrix helps trap both, air pollutants and intermediate byproducts, thereby promoting a complete degradation of pollutants. As a result, the concern of intermediates released into the atmosphere is reduced (Sopyan et al. 1996, Lackoff et al 2003, Cassar 2004, Berdahl and Akbari 2008). In addition, research by Cassar has shown that cement exhibits small amounts of photocatalytic degradation without TiO₂ caused from the hydroxides in the cement matrix. Thus, when added to concrete mix designs, TiO₂ increases its natural photocatalytic ability to one that is even higher than the TiO₂ alone suggesting a synergistic effect (Cassar 2004). Cassar attributes this synergy to both the high absorption capacity of the concrete matrix aiding complete degradation, as well as concrete's natural photocatalytic ability, making concrete an ideal substrate for photocatalytic materials (Cassar 2004). As a result, applications of TiO₂ in concrete have spread to road sound barriers, sidewalks, and highway overlays for air remediation.

Field applications of TiO₂ photocatalysts pavements are already in progress in Japan and Europe and are recently initiated in the United States. Japan has applied TiO₂ coatings to roadways and sound barriers amongst various cities such as Osaka, Chiba, Chigasaki, Suitama and Shinatoshin, covering at least 50,000 m² of surface area, and claiming at least 0.5 to 1.5 mmol/m² reduction rates (Osburn 2008). Full scale examples in Segrate, Italy, show photocatalytic durability lasted at least one year; however, longer duration tests are still in progress (Cassar 2004). Despite the availability of available studies, comparison between the experiments is challenging, due to the different variables, testing methods, and reporting methods (Osburn 2008).

2.3.2 Photocatalytic Pavement Synthesis

TiO₂ nanoparticles have been implemented in concrete pavements by applying a photocatalytic concrete pavement overlay, sprayed as a thin exterior film of suspended TiO₂ nanoparticles in a binding agent, or sprinkled TiO₂ nanoparticles on curing concrete (Hassan et al 2009). Yet the spray application and sprinkle techniques have higher concentrations of TiO₂ exposed on the surface, leading to slightly higher photocatalytic efficiencies, TiO₂ is most commonly incorporated into cement photocatalytic pavement overlays (Hassan et al 2009). Researchers prefer photocatalytic overlays due to their higher durability (Diamanti et al. 2008, Beeldens 2008). Not only is the mechanical strength of the TiO₂ modified cement increased, due to the pozzolanic activity of TiO₂ in hydrating cement and denser structure, but also any resulting abrasion from traffic results in new TiO₂ particles to be exposed (Lackhoff et al. 2003, Watts and Cooper 2008, Beeldens 2008).

The overlays of photocatalytic cement thicknesses have ranged from 0.3 to 8 mm (Beeldens 2008, Chen and Li 2007). Adding TiO₂ nanoparticles directly to the concrete mix produces the overlay. TiO₂ can be incorporated into concrete mixtures in two forms - as aqueous suspended nanoparticles, or as nanoparticle powders. Aqueous suspended particles are often smaller sizes, near to 88 nm in diameter, thus increasing its photocatalytic activity. The aqueous nanoparticle solution can be incorporated into a mortar overlay, substituting for some of the water requirements (Diamanti et al. 2008). TiO₂ powder particles sizes are usually larger than suspended ones, ranging between 150-400 nm in diameter, thus slightly decreasing its photocatalytic activity (Diamanti et al. 2008). However, when the sizes are mixed, there is a synergistic effect and the photocatalytic efficiencies are enhanced (Diamanti et al. 2008, Cassar et al. 2003). Research by Diamanti suggests an optimized photocatalytic layer design, suggested

as a mixture of 3% anatase powder and 2% anatase suspension versus cement weight (Diamanti et al. 2008). A similar effect can be achieved using a mixture of anatase (larger band gap) and rutile (smaller band gap) crystals (Zhao and Yang 2003). Optimum photocatalytic mixtures of anatase and rutile particles are already commercially available. For example, Degussa P25 uses at 20-30/70-80 rutile-anatase ratio (Strini et al. 2005, Zhao and Yang 2003).

TiO₂ is generally added as a percent of the cement weight. As expected, increasing TiO₂ concentrations increase photocatalytic pavement effectiveness. However, research shows that this relationship is not linearly dependent. Instead, increases at lower concentrations, such as 1% to 3%, have a greater impact on the improved photo-oxidation activity, compared to increases at higher concentrations, such as 3% to 6% (Watts and Cooper 2008, Strini et al. 2005). The increased concentration not only impacts the photocatalytic efficiencies, but also corresponds to the additional material costs. Italcementi's product TX, utilizing TiO₂ as a photocatalyst, is known to add as much as 20% to the cost of cement (Berdahl and Akbari 2008). As a result, when adding TiO₂ to current bulk materials, such as cement to minimize the additional costs, concentrations between 1-5% nanoparticles to cement are ideal (Watts and Cooper 2008, Strini et al. 2005).

Additional significant variables include mix design factors, such as the water cement ratio, size and type of aggregates, and cement aggregate ratio (Poon and Cheung 2007, Watts and Cooper 2008, Cassar et al. 2003). Not many experiments exist on optimization of the mix design for photocatalytic degradation. Poon's investigation on concrete blocks illustrates the impact of different aggregates and cement aggregate ratios on pavement photocatalytic properties. Poon found that recycled aggregates had higher NO removal than sand, possibly due to a higher porosity. Similarly, more porous specimens can be achieved by eliminating fine aggregates

below 300 μm . Consequently, removal of fine aggregates increased NO photodegradation by 4%. Furthermore, when glass was used as an aggregate, the photocatalytic properties were enhanced, due to the increased transmission of light. In addition, decreasing the cement content from a 1:2 cement aggregate ratio to a 1:3 ratio increased NO reduction efficiencies by 30% (Poon and Cheung 2007).

2.4 Environmental Factors Impacts on Photocatalytic Pavements Efficiency

There are many environmental factors that affect the photo-oxidation efficiency. Understanding these relationships is progressive and often varies by photocatalytic material thus making comparisons difficult. Nevertheless, known environmental factors consist of pollutant types, pollutant competition, pollution concentrations, air velocity, relative humidity, UV light intensity, and photocatalytic degeneration and regeneration.

2.4.1 Pollutant Types

Many different pollutants threaten our society in both the indoor and outdoor environments. Emissions from vehicle combustion are nitrogen oxides (NO_x), sulfur dioxide (SO_2), carbon monoxide (CO), and volatile organic compounds (VOCs) threatening both human health and the environment. For example, NO_x and VOCs pollutants are precursors to smog, especially prevalent on hot, sunny days (Berdahl and Akbari 2008). Furthermore, NO_x and SO_2 are the leading causes of acid rain, which not only destroys the environment by killing and reducing the biodiversity of forests and lakes, but also degrades our buildings (Poon and Cheung 2007, Thoma et al. 2008). Outdoor air also impacts indoor environments. NO_x and VOCs are both associated with sick building syndrome (Liu et al. 2008).

The photodegradation rates of each pollutant vary due to different absorption rates and reaction schemes. For example, VOCs – benzene – toluene - ethylbenzene –xylene (BTEX) all

showed various photo-steady-states and reaction rates (Ao et al. 2002). As a result, in research, there are continual attempts to describe the ability of titanium dioxide to degrade these pollutants through better understanding of the chemical kinetics.

2.4.1.1 Nitrogen Oxides

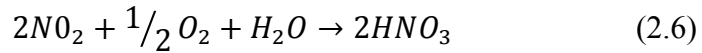
Nitrogen oxides are one of the most common pollutants researched for removal potentials. Nitrogen oxides have detrimental effects on the outdoor environment by promoting acid rain and effects on the indoor air quality, contributing to sick building syndrome. Further, roadway microenvironments contribute to 58% of NO_x emissions (Kuhns et al. 2004). For example, in Baton Rouge, NO_x emissions are typically 0.010 ppm. However the maximum can reach 0.152 ppm (DEQ 2006). Currently, EPA limits nitrogen dioxide to a 0.053 ppm recorded annual mean (EPA 2010^b). This regulation is expected to get stricter in the near future (EPA 2010^b).

The approved method of NO_x detection is chemiluminescence. Chemiluminescence occurs when light is emitted from a reaction, which in the case of NO_x is between NO and ozone. The amount of light emitted is proportional to the NO concentration. For nitrogen dioxide, an indirect approach is taken, since a catalytic converter must first reduce the nitrogen dioxide to nitric oxide in order to be measured. After catalytic conversion, the total NO measured corresponds to the NO_x concentration. Therefore, the nitrogen dioxide concentration is the difference between the total NO_x and the NO (EPA 1999, EPA 2007).

Titanium dioxide has the ability to remove NO_x , but the removal percentage differs due to many other known variables. For example titanium dioxide, when added to mortar, can remove up to 92% of NO_x in 7 hours of exposure from a 300 W lamp. A similar mortar layer was applied to a full-scale road in Segrate, Italy, with vehicle traffic of 1200 units per hour. The photocatalytic mortar application, on sunny days, resulted in a 50% reduction measure of NO_x

with stability of a year (Demeestere et al. 2008). Based on a summary of quantitative investigations published, a probable estimate of 200 m³ of air per day of NO_x can be removed from photocatalytic oxidation (Berdahl and Akbari 2008).

The oxidation of NO_x follows the reaction scheme below (Yu 2003):



Since NO₂ is an intermediate of NO, NO is used to test the photocatalytic ability for simplicity purposes (Yu 2003). Few studies have mentioned the amount of nitrates being released to water, stating only that the amount released is 10 times inferior to the original pollutant level (Picada 2001). The final product NO₃ is absorbed by concrete substrates, due to the alkalinity of concrete (Sleiman et al. 2009, Yu 2003). Furthermore it is theorized, but not confirmed, that the nitrates absorbed by the concrete react with the calcium hydrate Ca(OH)₂ in the concrete cement, neutralizing to Ca(NO₃)₂ and H₂O (Li and Qian 2009).

2.4.1.2 Sulfur Dioxide

Sulfur dioxide, another contributor to acid rain, has also been tested for photodegradation by TiO₂. Vehicle sources contribute up to 7% of total SO₂ emissions (Zhan et al. 2009). Ambient concentrations typical of Baton Rouge are 0.004 ppb for sulfur dioxide, with maximums reaching 0.076 ppb (DEQ 2006). EPA limits for sulfur dioxide is 75 ppb, recorded as a one-hour average (EPA 2010^a). Sulfur dioxide can be measured by the pulsed fluorescence SO₂ analyzer (EPA 1999). Studies have shown that absorption rates of SO₂ are 1.6-5 times higher than NO absorption. Despite the higher absorption rates, the SO₂ removal efficiency is not as promising as NO removal. In theory, SO₂ interacts with an active metal oxide, forming sulfates and sulfites

that are easily absorbed on the surface thus inhibiting the TiO₂ activation. This explains the higher absorption rate and lower removal rates of SO₂, compared to NO (Toma et al. 2006).

2.4.1.3 Volatile Organic Compounds

Volatile organic compounds (VOCs) threaten human health by causing cancer and the environment by means of greenhouse gases that increase global warming (Ao et al. 2004). VOCs are classified by the World Health Organization (WHO) as all organic compounds with boiling points in the range of 50 to 260°C, excluding pesticides. VOCs are typically higher for indoor environments as compared to outdoor environments. However, outdoor air is considered a source for indoor VOC pollution. Although the largest source of VOC pollution is from building materials, vehicles are still responsible for a 29% portion (Kuhns et al. 2004). For example, aromatic hydrocarbons including toluene, xylenes, ethylbenzene, trimethylbenzenes, and aliphatic hydrocarbons inclusive of octane, decane, and undecane are emitted from sources of gasoline and combustion (Wang et al. 2007). These petroleum derivatives are the most common VOCs found in both indoor and outdoor environments (Ao et al. 2004, Saarela et al. 2003). Typical ranges of individual indoor VOCs concentrations are between 5 µg/m³ to 50 µg/m³, which typically totals at concentrations higher than 50 µg/m³. The pollutants can be measured by a solid phase microextraction or analytical gas chromatography and quantified by mass selective detector (Saarela et al. 2003, Ao et al. 2004, Demeestere et al. 2008). According to a summary published of quantitative investigations, a probable estimate of 60 m³ of air per day of VOCs can be removed from photocatalytic oxidation (Berdahl and Akbari 2008).

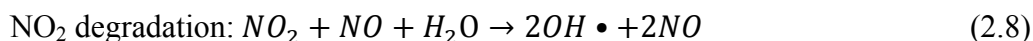
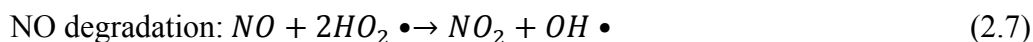
For VOCs the reaction rates are dependent on pollutant. Generally higher soluble compounds tend to have higher reaction rates. Thus, the ordering of conversion rates is as follows: alcohols and glycol ethers > aldehydes, ketones, and terpene hydrocarbons > aromatic

and alkane hydrocarbons> halogenated aliphatic hydrocarbons (Berdahl and Akbari 2008). More specifically, the benzene, toluene, ethylenzen, and o-xlyene (BTEX) removal efficiencies are ranked in increasing oxidation rates as benzene, toluene, ethylbenzene, and o-xylene (Strini et al. 2005, Demeestere et al. 2008). Although, VOCs are known to fully oxidize, some less desirable intermediates may be exposed (Berdahl and Akbari 2008). As a result, kinetic studies are becoming increasingly important; not only to understand the reaction rates, but more importantly to understand the intermediate chemicals.

2.4.2 Chemical Interaction and Competition

As shown, different reaction schemes exist by dependence on the pollutant. This results in different rates of photocatalytic degradation. Many pollutants are known to be able to photo-oxidize; however, interaction and competition of other pollutants is yet to be understood. In the presence of other chemicals, simultaneous photocatalytic oxidation reactions may inhibit or promote the removal rates. Pollutants such as SO₂ and BTEX are known to inhibit degradation of other pollutants while NO can enhance degradation. BTEX and SO₂ are known to inhibit degradation of formaldehyde. Both BTEX and SO₂ interfered with the formaldehyde degradation decreasing conversion by 10%. The SO₂, absorbed first into the TiO₂ surface, inhibits the absorption of formaldehyde. Similarly, BTEX competed for absorption with formaldehyde (Ao et al. 2004). BTEX also interferes with NO reduction (Ao et al. 2002). In contrary, NO_x enhances photodegradation of various pollutants. For example, NO_x increased the formaldehyde photodegradation rates by 5% at lower humidity levels and as much as 25% at high humidity levels (Ao et al. 2004). When BTEX combined with NO_x photo-oxidation, the largest enhancement was in the pollutants with lower reaction rates, benzene and toluene (Ao et

al. 2002). Theory suggests that the photodegradation of NO_x results in OH radicals, which can be employed for pollutant conversion (Eqns. 2.7 and 2.8) (Ao et al. 2004, Ao et al. 2002).



2.4.3 Concentration of Pollutants and Flow Rates

Research further supports that removal efficiency is a function of the quantity of pollutants and exposure periods. In research, flow rates have varied from 1 L/min to 6 L/min (Poon and Cheung 2007, Beelden 2006, Yu 2003, Chen and Li 2007). In the TiO_2 on roof tiles, when longer periods of gas residence with lower amounts of toluene gases are present, removal efficiencies increase, whereas with shorter periods and higher concentrations of toluene the efficiencies decrease (Demeestere et al. 2008). Similar results were concluded in experiments with indoor uses of TiO_2 photocatalytic oxidation of ethylene, formaldehyde, toluene, 1-butene, BTEX, and NO_x (Zhao and Yang 2003, Demeestere et al. 2008, Sleiman et al. 2009, Ao et al. 2002). For example, an increase in flow rate decreased the removal efficiency of toluene from 95% to 65% (Sleiman et al. 2009). The explanation provided was that an increase in flow tends to decrease the residence time with the photocatalytic reactor, while an increase in concentration of pollutants tends to increase the mass transfer rate and accumulation of final products (Sleiman et al. 2009, Demeestere et al. 2008, Ao et al. 2002). An accumulation of oxidation products on the surface inhibits continuous absorption of pollutants, potentially leading to deactivation of the photocatalysis (Ao et al. 2002). Thus, research points to the main use of titanium dioxide for small pollutant loads, similar to those found in indoor and outdoor air (Demeestere et al. 2008). Yet it is still important to locate photocatalytic surfaces near pollutants to ensure exposure (Beeldens 2006).

2.4.4 Relative Humidity

Water vapor has both negative and positive impacts, which is surprising, since water is a key source for hydroxyl radicals (Zhao and Yang 2003, Demeestere et al. 2008, Wang et al. 2007, Sleiman et al. 2009). As expected, the absence of water for some chemicals hinders the reaction rates common in toluene, benzene and formaldehyde photocatalytic oxidation. Surprisingly, water can also inhibit photocatalytic oxidation rates. Researchers suggest one explanation is that water particles compete with the pollutant molecules absorbed (Demeestere et al. 2008, Wang et al. 2007, Sleiman et al. 2009). Another thought is that the water forms one or more layers of film, which prevents the pollutant from reaching the TiO₂ layer (Sleiman et al. 2009). Thus, too much water interferes with reaction rates, which sometimes results in optimum humidity conditions (Wang et al. 2007).

Optimal humidity conditions were identified for removal of formaldehyde. At lower humidity levels, not enough radicals are present and at high percentages, competition impacts the amount of pollutants absorbed. Studies suggest that a 55% relative humidity for the optimal removal of formaldehyde is achieved (Liu et al. 2008). However, there seems to be a discrepancy in findings as to whether or not an optimal relative humidity level exists (Liu et al. 2008, Sleiman et al. 2009). For example, Sleiman's research on toluene photocatalytic oxidation showed no optimum relative humidity (Sleiman et al. 2009). In addition, some pollutants such as TCE exhibit only negative impacts by increasing water content (Zhao and Yang 2003). A second study on the reduction of formaldehyde did not find an optimal humidity level; instead, the conversion decreased from 80% to 54%, when the humidity level increased 2100 to 22000 ppmv (Ao et al. 2004). When the same humidity increase is subjected to toluene removal, efficiencies decreased from 72% to 19%. These discrepancies indicate that the impact of

humidity is not easy to describe. Impacts may differ by pollutant type, concentration, and possible other experimental factors (Ao et al. 2002).

2.4.5 UV intensity and Wavelength

It is clear that TiO_2 needs light as an energy provider to function and degrade any pollutants. Several experiments show that with the absence of light, photodegradation does not take place (Liu et al. 2008, Anpo and Takeuchi 2003, Poon and Cheung 2007, Nonami et al. 2004, Zhao and Yang 2003). Changing the light source impacts the wavelength and the photon flux. The wavelength is primarily responsible for the photocatalytic activity, while the intensity or photon flux impacts the rate of degradation. For TiO_2 , wavelengths smaller than 400 nm are required for irradiation, which corresponds to the UV spectrum from the sun. Higher intensities result in more photons produced, thus higher photocatalytic oxidation rates (Fujishima et al. 2000, Zhao and Yang 2003). The relationship between intensity versus photocatalytic oxidation rates is often a linear correlation. The rate of increase is dependent upon chemical pollutant. For example, when the irradiance changed from 0 to $1500 \mu\text{W}/\text{cm}^2$ the effects were a linear impact, increasing the oxidation activity drastically for o-xylene and ethylbenzene and slightly for benzene and toluene (Strini et al. 2005). In addition, photocatalytic oxidation of TCE was enhanced from 0.08×10^{-6} to $0.25 \times 10^{-6} \text{ mol/s g}$ as the light intensities increased from $0.08 \text{ mw}/\text{cm}^2$ to $0.45 \text{ mw}/\text{cm}^2$ (Zhao and Yang 2003). The intensity not only increases the activity rates, it impacts the intermediates formed. For example, more intermediates were formed using the germicidal lamps with higher intensities, when compared to lower intensities of black lamps (Zhao and Yang 2003).

2.4.6 Photocatalytic Degeneration and Regeneration

Another highly debated variable of photocatalysis is the possible degeneration of the photocatalytic properties. This may present the need of a way to restore the photocatalytic properties of TiO_2 (Nonami et al. 2004). Since TiO_2 is a catalyst and undergoes no change, it can theoretically be used indefinitely (Nonami et al. 2004). As a result, degeneration is caused by other factors such as interference of absorbed intermediates, and a decrease of catalytic surface from the build up of dirt, scum, gum, oil, and grease, especially if used in outdoor environments (Zhao and Yang 2003, Yu 2003). Thus, removal of these absorbed products can induce regeneration of photo-oxidation efficiencies.

In an indoor experiment on removal efficiencies of toluene over TiO_2 , there was no degeneration detected over the 48 hours tested, despite previous research findings of the deactivation of TiO_2 and even a slight, yellowish color change due to the accumulation of the absorbed species from photocatalytic oxidation of toluene (Sleiman et al. 2009, Demeestere et al. 2008). Therefore, research suggests that the degeneration and accumulation of products is may be a function of the time and concentration of pollutants present (Sleiman et al. 2009, Yu 2003). This could be why Sleiman, who used much lower concentrations in the 120 ppb versus 290 ppb, experienced no degeneration effects (Sleiman et al. 2009). Despite the debate, methods for regeneration are being investigated.

Regeneration theories include washing the surface with water simulating rain, blowing air, or surface burning (Beeldens 2008, Zhao and Yang 2003). Comparisons between the regeneration methods quickly eliminated air as a solution. For example, the TiO_2 on roof tiles, when flushed with clean air, had no change on the photocatalytic properties; however, simulating natural rain showed a 42% regeneration (Demeestere et al. 2008). To test the water theory,

Beeldens removed photocatalytic blocks from laboratory tests and field tests. The blocks removed for laboratory tests were removed over several different periods of time to represent different exposure levels. The photocatalytic efficiencies were recorded before washing the surface and after washing. The results showed that additional washing could play a significant role in improving the photocatalytic efficiencies to maintain durability (Beeldens 2008, Hunger et al. 2008). When tested in the outdoor environments, rainfall has shown an effect in regenerating the photocatalytic activities, similar to those of lab washing. As a result, some recommended that washing be completed at least every two months during the dry seasons (Yu 2002). However, water washing or rain has not been effective in exposure to adhesives and water insoluble contaminants. As a result, using a degreasing agent may be beneficial. Exposure to different contaminants is dependent on location, thus exposure to these contaminants can be controlled by locality (Yu 2003). Other proposed solutions from Zhao included burning the surface or water washing to eliminate intermediates and restore the active sites on the catalyst surface (Zhao and Yang 2003). Despite the debate, one thing upon which research agrees is that the durability of the catalytic activity must be proven for widespread implantation and possible regeneration techniques, i.e.) applying water wash must be evaluated if degeneration occurs (Berdahl and Akbari 2008).

2.5 Measuring Photocatalytic Pavement Efficiencies in Pollution Degradation

Measuring the photocatalytic efficiencies are most commonly completed by lab-simulated experiments. Lab experiments were first conducted to develop relationships of variables and determine feasibility of photo-oxidation. Since photocatalysis was a relatively new technology, standards did not exist. As a result, lab experiments ranged in a variety of setups. It was not until recently that standards, created in Japan, were adapted as ISOs.

2.5.1 Experiment Setups

Until recently there has not been a standard used for photocatalytic oxidation experiments resulting in a variety of experimental setups (Beelden 2006, Hunger et al. 2008, Strini et al. 2005). Through grouping the experimental setups by calculation techniques, two developed methods are found to evaluate photocatalyst activity; each requires a slightly different experimental setup schematic. The first setup, being the most common and easiest to use, is the single-pass or open flow-through reactor. The photocatalytic activity is measured by its reduction efficiency, calculated by the decrease in concentration between the outlet and the inlet of the reactor as shown in Equation 2.9.

$$\eta = \frac{C_{in}-C_{out}}{C_{in}} \quad (2.9)$$

where,

η = photocatalytic reduction efficiency

C_{in} = the inlet concentration

C_{out} = the outlet concentration

To avoid errors from material absorption, the inlet concentration is often replaced with the equilibrium concentration before irradiation. This change is shown in Equation 2.10.

$$\eta = \frac{C_o^*-C^*}{C_o^*} \quad (2.10)$$

where,

η = photocatalytic reduction efficiency

C_o^* = the initial equilibrium concentration (no lights)

C^* = the equilibrium concentration (lights)

The advantage of this method is that a single pass of gas flows at various concentrations. However, disadvantages to this method are the a) resulting errors at low concentration levels due to the small difference, b) absorption of pollutants on the reactor, and c) pollutant concentration over the substrate is not uniform (Strini et al. 2005). An example of the single-pass open flow reactor experiment setup is drawn in Figure 2.2, a diagram of the experimental setup used by Yu 2003.

The second, more complex approach uses recirculation, often referred to as the static method. The static method uses a closed circuit of air circulation to measure the abatement of NO_x over time (Strini et al. 2005, Hunger et al. 2008). This experimental setup follows the schematic shown in Figure 2.3. Unlike the single-pass open flow reactor setup, the recirculation setup evaluates the photodegradation half-life (Zorn et al. 2000). Regardless of the experimental setup, the photocatalytic byproducts may also be measured for verification of degradation results (Strini et al 2005).

2.5.2 Equipment

Both experimental setups require the following equipment: pollutant source, photoreactor, and pollutant analyzer. For the open, flow-through reactor, the pollutant source is usually a compressed gas cylinder of the particular pollutant compound of interest (Poon and Cheung 2007, Yu 2003). Since the pollutant is of such high concentrations compared to normal ambient concentrations, the pollutant is mixed with zero air, or air free of pollutants, for dilution. Mass flow controllers are used to control both the desired outlet concentration and flow rate to the photoreactor. Often a calibrator is used for this purpose. The photoreactor houses the substrate in a controlled environment for the reaction to occur. Then the analyzer measures the outlet

stream from the controlled environment of the photoreactor. Humidifiers are also incorporated into the above schematics to test the impact of humidity (Hunger et al. 2008).

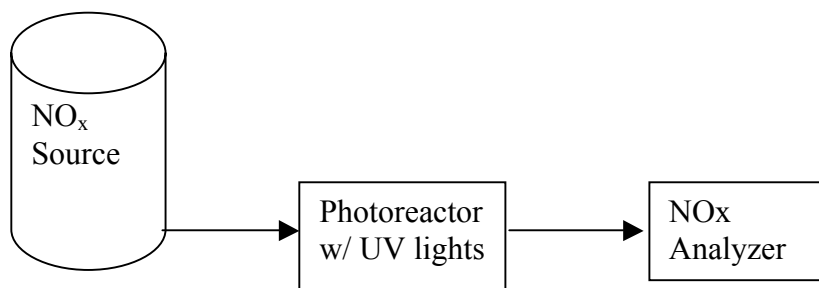


Figure 2.2 Single Pass Test Schematic (modified from Yu 2003).

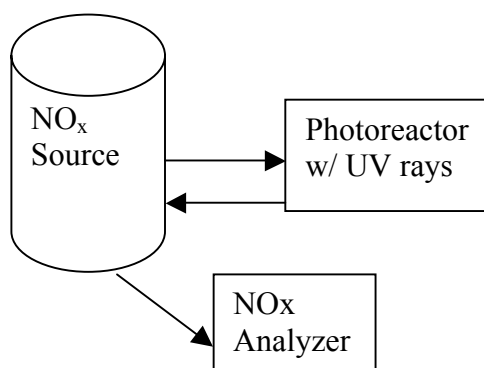


Figure 2.3 Recirculation Test Schematic (modified from Zorn et al. 2000)

2.5.3 Photoreactor

The photoreactor is an enclosed environment housing the photocatalytic substrate. It has an inlet and outlet for sampling ports to monitor the pollution concentration. Typically, chambers are made of stainless steel or pyrex glass with rubber sealant to protect against pollution absorption and leakage (Poon and Cheung 2007, Beeldens, Hunger et al. 2008). However, in efforts to reduce costs, wooden photoreactors lined with aluminum foil have also been effective (Chen and Li 2007). Choosing materials compatible with the pollutant gas is essential, since many

pollutants are highly reactive (EPA 1999). The size of the photoreactors ranged from as little of 1 mL to as large as 100 L volume capacity. Smaller photoreactors were most likely to be made of glass cylinders or pyrex tubing, whereas the larger photoreactors used a metal container (Noguchi et al. 1998, Beeldens 2006). The light source can either be inside or outside of the photoreactor, often dependent upon the photoreactor size. Light sources outside the photoreactor have the advantage of being able to modify the distance, such that the intensity can be varied. In these setups, it is important to have a UV transparent glass top to allow passage of the UV rays (Nimlos et al. 1996, Noguchi et al. 1998, Piera et al 2002, Kim et al. 2002, Hunger 2008). Light sources inside the photoreactor often heat the photoreactor. To mitigate the heat gains, fans were often used for cooling (Hunger et al. 2008).

2.5.4 Light Source

Since the reaction is dependent on the wavelength of the light, the light source chosen is important. Light sources vary from mercury lamps, germicidal lamps, solar lamps, UV-A lamps and metal halides, all with differently corresponding wavelengths. Fluorescent lamps typically have wavelengths of 420-650 nm with three intensity peaks at 460, 560, and 600 nm, whereas UV-A emits wavelengths within 300-400 nm with a maximum intensity peak at 345 nm (Hunger 2008). Florescent lamps are one of the most popular light sources, with wavelengths between 300-460 nm and maximum wavelengths of 365 nm (Beeldens 2006). With phosphor coatings, black lights emit only UV-A light, while the harmful, short-wave UV-B and UV-C lights are absorbed (Fujishima and Zhang 2006). Maximum wavelengths emitted for black lights are generally smaller, near 355 nm (Yu 2003). The wavelength required for TiO₂ irradiation is between 300 to 365 nm, thus UV-A sources are recommended. The sun emits 1-2 mW/cm² in wavelengths below 350-400 nm (Zhao and Yang 2003). Therefore, the recommended intensity

is near 1 mW/cm², which can be measured by a UV-A radiometer (Zhao and Yang 2003, Kim and Hong 2002, Piera et al. 2002, Sopyan et al. 1996).

2.5.5 Humidity Controller

The humidity may be controlled in many ways. For simplicity, many experiments used a natural, room relative humidity. Meanwhile, to increase the humidity, air is passed through either a water bath or a humidifier (Dalton et al. 2002, Sleiman et al. 2009). A humidity sensor is placed in the photoreactor to note and record the relative humidity (Sleiman et al. 2009).

2.5.6 Gas Analyzer

The gas analyzer is determinant on pollutant type and concentration. The sampling intervals can either be continuous or discrete, depending on the gas analysis techniques available. For NO_x portable analyzers are available for continuous concentration monitoring at ambient air conditions (Yu 2003). The approved technique for EPA standards in NO_x ambient air testing is chemiluminescence (EPA 1999). SO_x continuous monitoring analyzers are also available for concentrations of ambient air conditions. The approved EPA technique is the pararosaniline method, which is a wet chemical method, rather than a continuous monitoring system (EPA 1999). An equivalent method for continuous monitoring is fluorescence (EPA 2007).

Since VOCs are not called out on the National Ambient Air Quality Standards, there are no reference methods required (EPA 1999). A gas chromatography flame ionization, gas chromatography, mass spectrometry, and Fourier transform infrared spectroscopy are all recognized techniques (EPA 2007). These techniques are not always continuous and portable devices. As a result, multibed solid sorbent sampling tubes are required; in this case, sample intervals must be determined (Sleiman et al. 2009). Sampling intervals in previous experiments

for various VOC detection were 10 min, 20 min, 30 min, and 1 hour intervals (Sopyan et al. 1996, Wang et al. 2007, Kibanova et al. 2009, Sleiman et al. 2009).

2.6 Testing Standards for Performance of Photocatalytic Materials

More current research follows the experimental setup standards first defined by the Japanese, the JIS TR Z 0018 “Photocatalytic materials-Air purification test procedure” standards. The creation of the JIS TR Z 0018 is the first part of many standards to be developed for testing photocatalytic products. For example, the Japanese standard was adapted for the ISO TC 206/SC N, “Fine ceramics (advanced ceramics, advanced technical ceramics) – Test method for air purification performance of photocatalytic materials – Part 1: Removal of nitric oxide” (Beeldens 2006, JIS 2004). The method is meant to be reproducible for a variety of materials, such as building materials and road construction materials (JIS 2004).

The standard specifies a specific procedure for evaluating the photocatalytic performance in removal of nitrogen oxides, yet photocatalytic oxidation can occur for a variety of pollutants such as dyes, organics, and inorganics. NO is regarded as the ideal model pollutant for determination of guidelines and testing standards. This is because dyes tend to exhibit limited decomposition without catalysts. VOCs are more resistant to UV degradation, decomposing to CO₂ and H₂O. VOCs are the ideal model pollutant for indoor situations; however, for outside applications -especially in concrete- the value of degradation measured can be inflated, due to the naturally occurring carbonation of concrete. In addition, VOCs often represent toxic chemicals, which are difficult to handle (Hunger et al. 2008).

2.6.1 Experimental Setup

The experimental setup following the JIS and ISO standards follow the single pass flow-through method, previously described and illustrated in Figure 2.2 (Beeldens 2008). The photoreactor

size is determined such that it is 3 times the length of the sample and at least 5 mm of air space is provided above the sample. To avoid turbulence in the airflow, the test specimen should be centered in the photoreactor. Fluorescent lamps with wavelengths between 300-400 nm or an xenon lamp with optical filters to block the lower radiation are acceptable light sources. The light source shall be placed outside of the photoreactor at an adjustable distance to obtain an irradiance of 10W/m^2 measured by a UV-A photometer. Therefore, the window must not absorb light longer than 300 nm, thus quartz or borosilicate glass is recommended. A chemiluminescent NO_x analyzer measures the concentration of pollutant. Proper calibration steps must be followed in accordance to the specified standards (JIS 2004).

2.6.2 Testing Procedure

The test piece shall be pretreated and stored in an airtight container if testing does not immediately proceed. The pretreatment process entails irradiation of the test piece with UV light for at least five hours to remove any organic matter using an irradiance of 10W/m^2 or higher. Then the material is washed in purified water for more than two hours and air dried at room temperature, until a constant weight is achieved (JIS 2004).

To begin the NO_x removal test, the specimen first shall be exposed to pollutants under dark conditions for at least 30 minutes to determine the adsorption rate. The flow rate of the inlet gases shall be 3 L/min with a 1.0-ppm concentration of NO at 50% humidity and room temperature. The second stage with the light source on may start as soon as the outlet concentration equals the inlet concentration. The NO and NO_2 concentrations shall be continuously monitored for at least five hours under irradiation. After five hours, photoirradiation may be stopped and the gas supply is changed to the zero-calibrated gas until the concentration of NO_x is zero (JIS 2004).

Since NO_x removal results primarily in nitrate ion and nitrite ion, washing with water is the suggested removal technique to restore the photocatalytic efficiencies. After elution, the recovery from washing is calculated. To wash the sample, the material is immersed in purified water for one hour and the volume is recorded. The procedure is repeated, using a new sample of purified water of the same volume as the first. The pH of the water after washing shall be measured to calculate the amount of NO_x eluted from the test piece. Standard equations, a diagram of the equipment setup, and a typical graph are provided by the standards as well (JIS 2004).

2.6.3 Calculations

After the test, the net amount of NO_x (mol) removed is calculated. The net amount of NO_x removed is the summation of the total NO adsorbed and the amount of NO removed, minus any NO₂ that is formed and the amount desorbed. All of these can be calculated from a typical graph of concentration versus experiment time. Equation details for each amount are provided in the JIS standards (JIS 2004).

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CHAPTER 3

EVALUATION OF THE ENVIRONMENTAL EFFECTIVENESS OF TITANIUM DIOXIDE PHOTOCATALYST COATING FOR CONCRETE PAVEMENT¹

3.1 Introduction

Major forces like climate change and rapid depletion of resources have resulted in initiating a strong movement toward sustainability, as consumption of raw materials has increased dramatically and air quality in large, metropolitan areas has been linked with serious health hazards to the public. Road microenvironments contribute to 29% of the volatile organic compounds (VOCs), 35% of the nitrogen oxides (NO_x), and 58% of the carbon monoxide (CO) emitted in the United States (EPA 1994, Kuhns et al. 2004). These concentrations are often higher in cities where trends of urban development and increased traffic volumes add to emissions, while street canyon conditions inhibit their dispersion, resulting in high ground level pollutant concentrations. The emissions of harmful air pollutants associated with highway operations often surpass the concentrations from industrial sources, making traffic emissions the primary source of urban air pollution (Berkowicz et al. 2006, Baldauf et al. 2008, Thomas et al. 2008, Chen et al. 2008,). Consequently, many adverse health effects are being linked to areas within 100 m from roads where pollution is not fully diluted. This affects more than 35 million Americans who live within this proximity limit, thus making transportation pollution a major concern (Thomas et al. 2008).

One potential solution for pollution remediation may be heterogeneous photocatalysis in which the natural decomposition process of harmful air pollutants is accelerated. Photocatalyst compounds such as titanium dioxide (TiO₂) can trap and oxidize organic and inorganic particles

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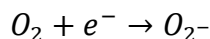
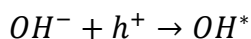
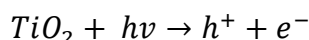
in the air removing harmful air pollutants such as NO_x and VOCs in the presence of UV light (sunlight) (Beeldens 2008). In addition, their super-hydrophilic properties allow them to self-clean in the presence of rain (Fujishima and Zhang 2006). Photocatalytic compounds can be utilized to construct air-purifying concrete by integrating titanium dioxide particles into the surface layer of highway pavements. Extensive research in recent years has shown that the properties of these particles to self-clean and to decompose pollutants are maintained over time and can even be enhanced when incorporated in concrete mix designs (Poon and Cheung 2007). In addition, concrete pavement's large surface area is in close proximity to pollutants in urban areas, which makes it an ideal substrate for heterogeneous photocatalysis air remediation (Beeldens 2008).

Self-cleaning, air-purifying concrete pavement is a rapidly emerging technology that can be constructed using air-cleaning agents with super-hydrophilic and photocatalytic capabilities, such as titanium dioxide. Although this technology has the potential to support environmentally friendly road infrastructure, a number of design and operational parameters may affect its effectiveness and need to be evaluated. To this end, the objective of this study was to evaluate the environmental and mix design parameters that may affect the effectiveness of the TiO₂ coating's environmental performance. To achieve this objective, an experimental program was conducted in which the effects of relative humidity level, pollutant flow rate, and mix design parameters, including contents of TiO₂ and aggregate sizes, were investigated. In addition, the abrasion and wear resistance properties of TiO₂ coating were evaluated.

3.2 Background

Titanium dioxide used in heterogeneous photocatalysis was first discovered by Fujishima and Honda in Japan during the 1970s (Fujishima and Honda 1972). However, it was not until the

middle of the 1990s that interest was expressed in using this technology in the area of air purification. The key to the photocatalytic reaction is the formation of electron-hole pairs initiated by energy that is greater than the band gap energy, which can be supplied by common UV light sources, such as sunlight. Once irradiated, titanium dioxide forms highly oxidizing holes and photo-generated electrons resulting in hydroxyl radicals and superoxides, respectively (Fujishima et al. 2000):



The holes, h^+ , and the electron pair, e^- , are the product of powerful oxidizing and reductive agents (Zhao and Yang 2003). The hydroxyl radicals and superoxides have been proven to play an important role in the photodegradation reactions (Fujishima and Honda 1972). The hydroxyl radicals, OH^* , are strong oxidants that rapidly decompose organic and inorganic compounds (Hunger et al. 2008). Thus, rather than just absorbing pollutants, common to traditional air purification methods, pollutants are decomposed to nonhazardous waste products with little energy requirements (Zhao and Yang 2003).

Titanium dioxide crystallizes in three forms, anatase, rutile, and brookite, in which anatase and rutile are the two commonly used types as photocatalytic (Beeldens 2008). Research has shown that titanium dioxide in the anatase phase is a more powerful photocatalyst than rutile in environmental purification (Bilmes et al 2000). However, the most abundant type is rutile, and is therefore, the most common type used in industrial applications. This type of titanium dioxide particles is low-cost and can remove a wide range of organic contaminants (Benedix et al. 2000). Other factors affect the photo-oxidation efficiency, including the type of substrate

material, the application method for the photocatalytic compound, the concentration of photocatalytic, the pollutant type, the pollutant concentration and flow rate, the interaction between multiple pollutants, the relative humidity, intermediates, UV light intensity, and photocatalytic degeneration and regeneration (Poon and Cheung 2007, Watts and Cooper 2008).

Although the potential of using TiO_2 as an air purifier in urban and metropolitan areas has been recently recognized in literature, practical applications have been limited to building facades and statues (Poon et Cheung 2007). Titanium dioxide has also been evaluated and patented as environmentally friendly cement (TioCem), architectural concrete (white cement), facade to buildings, and as concrete tiles (Yoshihiko et al. 2002, Heidelberg 2008). Being produced in a powder form, a number of research studies have suggested to use it in a thin film form and to apply it as a coating or slurry to various types of substrates, including concrete pavement surfaces (Sopyan et al. 1996). However, there is a need to determine the efficiency of photocatalytic technology under various operational and design conditions, in order to optimize its environmental purification performance in pavement applications.

3.3 Experimental Program

The objective of the experimental program was to evaluate the effects of operational and mix design parameters on the environmental performance of titanium dioxide coating. For this purpose, titanium dioxide concentration, aggregate gradation, flow rate, and relative humidity were varied and the environmental performance of the coating was measured, using a newly developed laboratory setup. This setup included a photocatalytic testing device, referred to as a photoreactor that creates an enclosed, controlled environment where the light and the atmosphere can be simulated. Testing was conducted for a total time of five hours; however, the

photocatalytic process was only started after 30 minutes from the beginning of the test to ensure that steady concentration was reached in the environmental chamber.

3.3.1 Laboratory Samples and Materials Tested

The concrete base design adopted in this study was an ordinary concrete mix design, typically used in Louisiana in order to achieve a compressive strength of 41 MPa. The substrates were placed into molds with dimensions of 305 mm x 381 mm x 25.4 mm and a curing compound was applied. A seven-day curing period was allowed before demolding and applying the photocatalysis surface coating. The photocatalytic surface coating consisted of ultrafine titanium dioxide, cement, water, and aggregate filler. A commercially available titanium dioxide nanomaterial (Cristal Millennium PC105) was used at a content of 3% and 5% per cement weight. The selected filler was sand with a maximum nominal size of 1.18 mm; see Figure 3.1.

The experimental test matrix varied the titanium dioxide content (3% and 5%) and the aggregate gradation (with fines and without fines) resulting in four different surface mix designs; see Table 3.1. Three replicates were produced for each test condition to account for variability. Surface mixes produced with no fines were prepared by removing all fines 300 μ m or smaller from the sand source. The surface mixture was prepared at a water-cement ratio of 0.6 and was applied to the concrete surface as a 10 mm thick coating, Figure 3.1.

3.3.2 Environmental Test Setup

The test set up was adapted from the Japanese standard JIS TR Z 0018 “Photocatalytic materials – air purification test procedure” in which the equivalent ISO is ISO 22197-1 (2007) “Fine ceramics (advanced ceramics, advanced technical ceramics)—Test method for air-purification performance of semiconducting photocatalytic materials—Part 1: Removal of nitric oxide” (JIS 2004). The developed experimental setup consisted of a pollutant source, zero air source,

calibrator, humidifier, photoreactor, and chemiluminescent NO_x analyzer, as shown in Figure 3.2. The setup simulates different environmental conditions by allowing for control of light intensity and air humidity. The pollutants are introduced through an inlet jet stream to the photoreactor, a photocatalytic testing device. A zero air generator is used to supply the air stream, which is passed through a humidifier to simulate the desired humidity level.

The photoreactor creates an enclosed, controlled environment, where the light and the atmosphere can be simulated. Fluorescent lamps, attached to the photocatalytic device, are used to imitate natural sunlight radiation required for photocatalytic activity. The pollutants measured from the recovered air before and after the photoreactor allowed for determination of the absorbed level of pollutants. In this study, nitrogen-oxide removal efficiency was measured, using the Thermo 42i chemiluminescent NO_x analyzer. The Thermo 146i Gas calibrator was used to supply a defined concentration of gas for the experimental setup at a controlled flow rate. Nitrogen oxide (NO) was blown over the surface at a concentration of 410 ppb at flow rates of 9 l/min, 5 l/min, and 3 l/min. All tests were conducted at room temperature, while the relative humidity was varied to three different levels, 30%, 50%, and 80%.

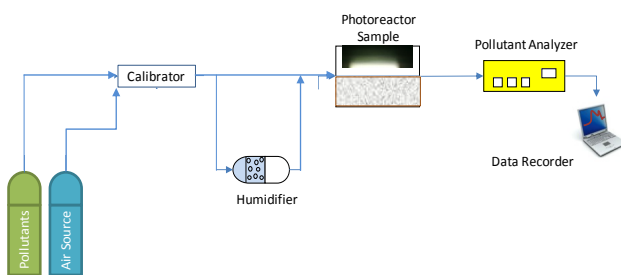
The photoreactor was made of Teflon and 316 stainless-steel, which are approved materials, according to the Environmental Protection Agency (EPA) and the Japanese Industrial Standard (JIS), to ensure gas compatibility. To accommodate larger sample sizes, the photoreactor was modified for samples as large as 305 mm x 380 mm x 25 mm. To make the photoreactor more cost effective and easier to manufacture, the support was made out of plywood and the interiors were lined with a Teflon coating. The glass window of the

Table 3.1 Evaluated Surface Mixtures in the Experimental Program

Sample Notation	TiO ₂ Percent	Aggregate Gradation
5N	5%	Without Fines
5F	5%	With Fines
3N	3%	Without Fines
3F	3%	With Fines



Figure 3.1 Illustration of the Pouring and Sample Preparation

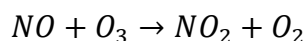


(a) **Figure 3.2** Illustration of the Experimental Laboratory Setup (b)

photoreactor was made of borosilicate glass to ensure passage of UV rays. The UV ray light source was two 20 W fluorescent lights mounted outside of the photoreactor. This allowed the UV intensity to be adjusted by changing its distance from the light source. In addition, this eliminated the need of a fan inside the photoreactor to reduce the heating effect from the lamps. The photoreactor uses funnel inlets and outlets and is three times longer than the sample size to ensure laminar flow.

3.3.3 System Calibration

Before testing, the Thermo 42i was calibrated in accordance to EPA calibration procedures, using the gas phase titration (GPT) alternative. This technique uses the rapid gas phase reactions between the NO and O to produce NO₂, using the following chemical reaction:



The Thermo 146i gas calibrator follows this principle to supply known concentrations of NO and NO₂, used in the NO_x analyzer. The NO_x analyzer was calibrated at five different spans for NO calibration and four different ozone settings for NO₂ calibration to confirm linearity and ozone converter efficiency. The calibration points were chosen between the accuracy ranges that were set from 0 and 500 ppm, typical settings of ambient air monitoring equipment.

3.4 Results and Analysis

3.4.1 Mix Design Parameters Test Results

Figure 3.3 presents the NO removal efficiency for the four mix types evaluated in this study (5% TiO₂ with fines, 3% TiO₂ with fines, 5% TiO₂ without fines, and 3% TiO₂ without fines). Past researchers have suggested that a coating with less fine particles would result in higher porosity, and therefore, improves NO removal efficiency (Poon and Cheung 2007). As shown in Figure

3.3, the coatings prepared without fines had predominantly greater NO removal efficiencies than the coating prepared with fines. It is also a common belief that the higher the TiO₂ content, the higher the NO removal efficiency will be. Results presented in Figure 3.3 show that this relationship holds true; however, it is not clear whether the observed improvement in NO removal efficiency justifies the increase in cost.

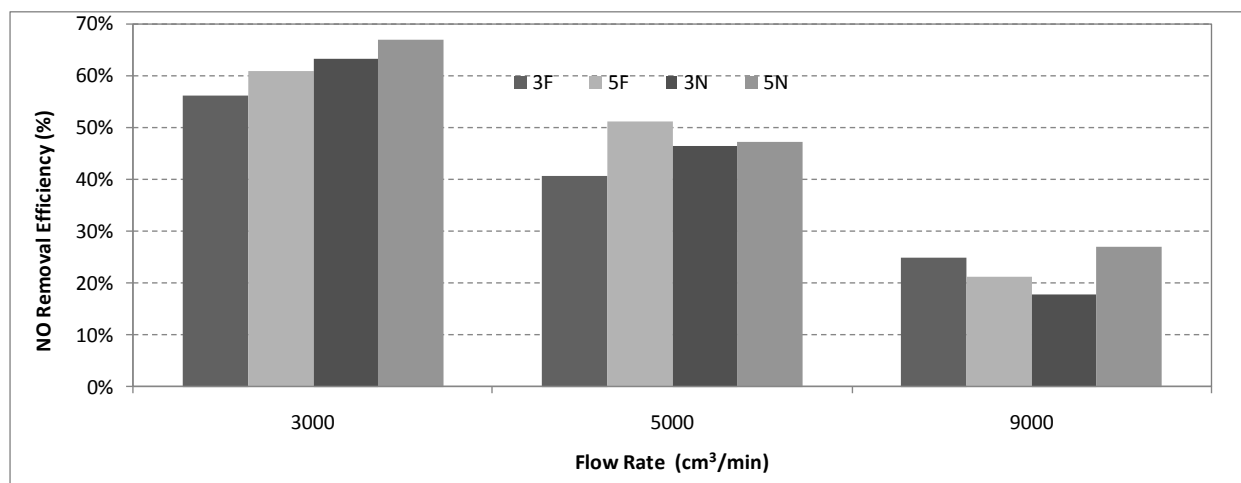


Figure 3.3 NO Removal Efficiency for the Different Mix Designs

3.4.2 Environmental Parameters Test Results

Figure 3.4 illustrates the variation of the NO removal efficiency with the relative humidity. As shown in this figure, as the humidity level increased, the NO removal efficiency decreased. Research has reported that water vapor can have both negative and positive impacts on the environmental performance of TiO₂. Although water is a key source for the hydroxyl radicals, researchers suggest that water particles may compete with the pollutant molecules absorbed, which could be responsible for the trend exhibited in the NO removal efficiency for this factor.

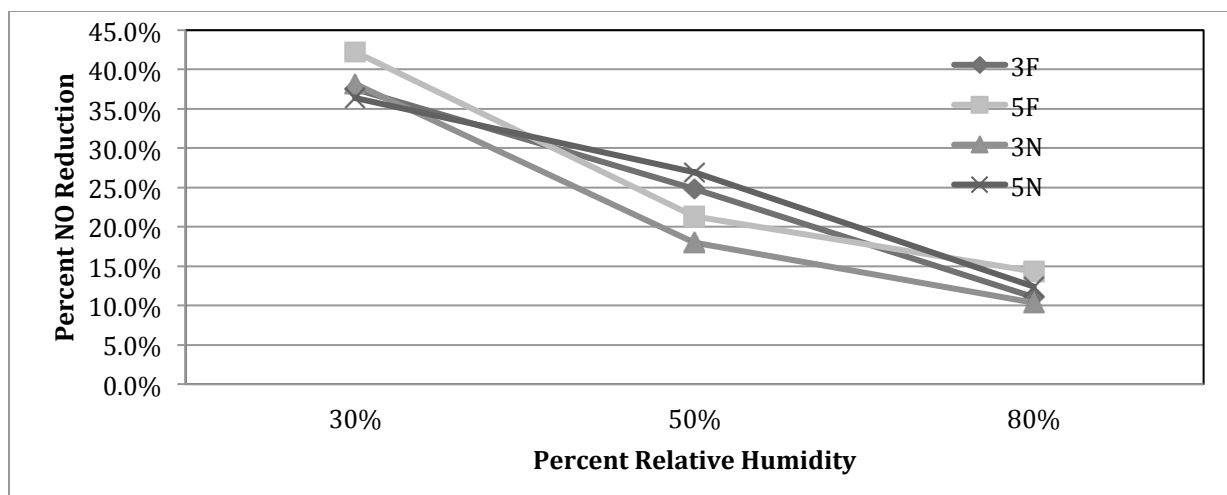


Figure 3.4 Impact of Percent Relative Humidity on NO Reduction

The flow rate correlates to the NO resident time, which can be calculated as the flow rate divided by the volume of the photoreactor. In this case, three resident times were evaluated, 7.1 min, 4.3 min, and 2.4 min correlating to a flow rate of 3, 5, 9 l/min, respectively. Table 3.2 presents the variation of the NO removal efficiency with the mix design of the coating and the flow rate for the introduced pollutants. The highest removal rates exhibited were for the samples with 5% TiO₂ with no fines (i.e., 5N). Figure 3.5 illustrates the variation of NO removal efficiency in relation to the flow rate for the samples with 3% TiO₂ with no fines. As the flow rate increased, the NO removal efficiency decreased. This was expected, since as the resident time decreases, it allows less time for the pollutants to be absorbed by the photocatalytic compound.

Table 3.2 Percent NO Reduction per Flow Rates

Sample	Flow Rate (cm ³ /min)		
	3000	5000	9000
3F	56.4%	40.9%	24.9%
5F	61.1%	51.2%	21.4%
3N	63.3%	46.7%	18.0%
5N	67.0%	47.3%	27.0%

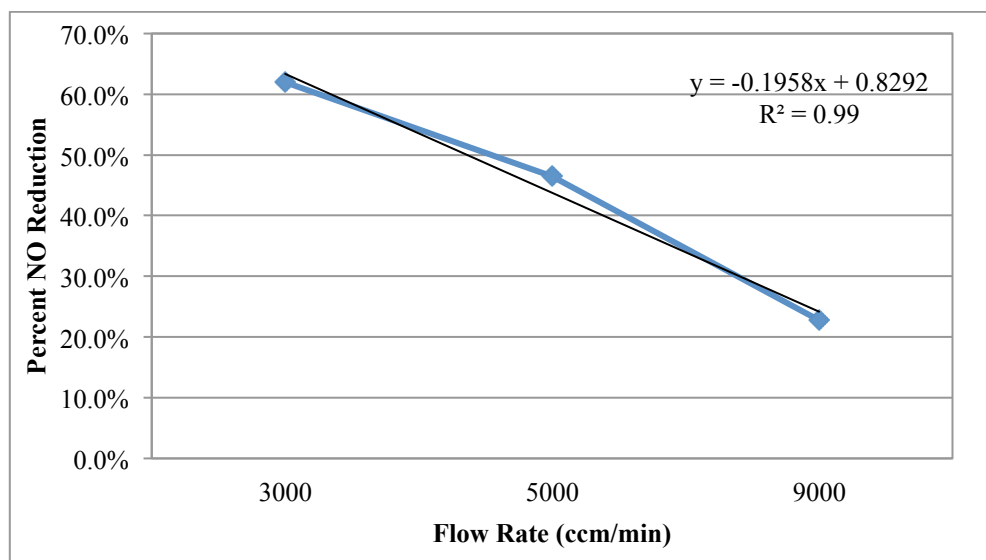


Figure 3.5 Impact of Flow Rate on NO Reduction

3.4.3 Durability of the Photocatalytic Coating

The wear resistance properties of the titanium dioxide surface layer were measured, using an accelerated loading test. A Hamburg type of Loaded Wheel Tracking (LWT) tester manufactured by PMW, Inc. of Salina, Kansas, was used in this study. This test is considered a torture test that produces damage by rolling a 703 N steel wheel across the surface of the coating at 25°C for 20,000 passes at 56 passes per minute. The rut depth at 20,000 cycles is measured and used as an indicator of durability. Figure 3.6 presents the measured rut depth and its variation with the increase in the number of wheel cycles for three specimen types (control with no coating, coating with no fines at 3% TiO₂, and coating with no fines at 5% TiO₂). As shown in this figure, the measured rut depth for the three specimens was minimal (less than 1mm) indicating that the use of the coating did not appear to affect the wear resistance of the surface. It is noted that this test is usually employed for asphalt surface; failure is defined at a rut depth of 6mm after 20,000 cycles at 50°C. Therefore, it appears that the produced coating provides

acceptable resistance to wear. More details about the durability of the coating have been presented elsewhere (Hassan et al. 2009).

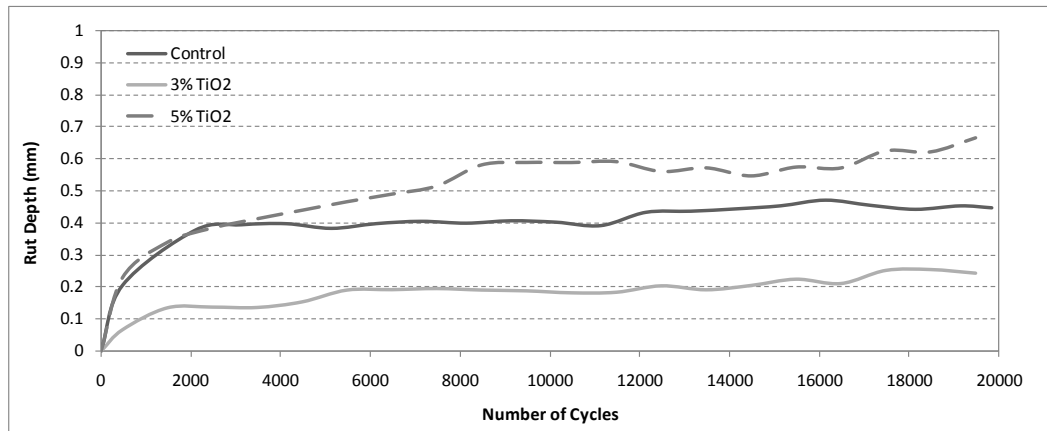


Figure 3.6 Measured Rut Depth in the Loaded Wheel Test

3.5 Conclusions

Self-cleaning, air-purifying concrete pavement is a rapidly emerging technology that can be constructed using air-cleaning agents with super hydrophilic photocatalyst, such as titanium dioxide (TiO₂). Although this technology has the potential to support environmentally friendly road infrastructure, a number of design and operational parameters may affect its effectiveness and need to be evaluated. The objective of this study was to evaluate the environmental and mix design parameters that may affect the effectiveness of the TiO₂ coating's environmental performance. To achieve this objective, an experimental program was conducted in which the effects of relative humidity level, pollutants' flow rate, and mix design parameters including contents of TiO₂ and aggregate sizes were investigated. Based on the analysis conducted, the following conclusions may be drawn:

- The mix design without fines achieved the highest photodegradation rates.
- The increase from 3% to 5% TiO₂ resulted in little improvement in the NO removal efficiency; however, cost-effectiveness of this improvement needs justification.

- The NO removal efficiency decreased with the increase in humidity level. This may be because water inhibits absorption of NO by the photocatalytic compound and thus hampers the photodegradation rates.
- As the flow rate increased, the percent NO removal efficiency decreased. This was expected since as the resident time decreased, it allowed less time for the pollutants to be absorbed by the photocatalytic compound.

Based on the results presented in this study, further research is recommended to consider factors such as coating application methods and influence of other pollutants. Furthermore, full-scale research is needed to validate the efficiency of the technology in the field.

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CHAPTER 4

LABORATORY INVESTIGATION OF THE EFFECT OF MIXED NITROGEN DIOXIDE (NO₂) AND NITROGEN OXIDE (NO) GASES ON TITANIUM DIOXIDE PHOTOCATALYTIC EFFICIENCY IN CONCRETE PAVEMENTS²

4.1 Introduction

NO_x is a group of highly reactive gases, nitric oxide (NO) and nitrogen dioxide (NO₂), originating from high temperature fuel combustion (EPA 2010). Many negative impacts are associated with NO_x emissions, such as formation of tropospheric ozone, urban smog, acid rain, and fine particle pollution, which can cause many adverse health effects (Jimenez et al. 1999). As a result, NO_x is one of the six major pollutants listed as a “criteria pollutant” as part of the ambient air quality standards required by the 1970 Clean Air Act (Tao et al. 2010).

The Clean Air Act has been successful in decreasing NO₂ concentration by 48% from 1970 to 2002 (Tao et al. 2010). However, in spite of the overall reduction in NO_x emissions nationwide, high short-term concentration of this pollutant is raising new concerns. Mobile sources such as traffic emissions contribute up to 58% of NO_x pollution emitted in the US (EPA 2010). This figure increases in areas with high traffic density (Jimenez et al. 1999). Compared to ambient concentrations, in-vehicle microenvironment NO_x concentrations are 2-3 times higher, and near-roadway microenvironment NO_x concentrations are 30-100% times higher (EPA 2010). Numerous studies have shown that even these short-term high concentrations can have negative impacts on human health (McConnel et al. 2010).

Self-cleaning, air-purifying concrete pavement is a rapidly emerging technology that can be constructed using air-cleaning agents with photocatalytic capabilities such as titanium dioxide

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(TiO₂). This technology is especially promising for city roads, where trends of urban development and increase in traffic volumes add to emissions while street canyon conditions inhibit their dispersion, resulting in high ground level pollutant concentrations. Recent research has shown that a thin TiO₂ surface coating is able to remove a significant portion of NO pollutants from the atmosphere when placed as close as possible to the source of pollution (Dylla et al. 2010). Hassan et al. (2010) evaluated three methods of application for TiO₂ to concrete pavement, a cementitious-based ultra-thin coating, a water-based titanium dioxide solution (PT), and sprinkling TiO₂ to the fresh concrete surface before hardening. Titanium dioxide incorporated into a cementitious ultra-thin surface layer was more durable, while maintaining high environmental efficiencies before and after abrasion and wear. However, the effectiveness of photocatalytic compounds such as titanium dioxide in degrading mixed NO₂ and NO gases has not been evaluated.

The objective of this study was to evaluate the environmental effectiveness of TiO₂ coating in photodegrading mixed NO₂ and NO gases from the atmosphere. To achieve this objective, an experimental program was conducted in which the effects of the ratio of NO₂ and NO gases, relative humidity level, pollutants' flow rate, and mix design parameters, including contents of TiO₂ and aggregate sizes, were investigated.

4.2 Background

Over the years, NO_x emissions near roadways have been reduced (Carslaw 2005, Minoura and Ito 2010). Although decreasing NO_x emission trends are confirmed, NO₂ concentrations have remained relatively constant. Consequently, the ratio of NO₂/NO_x has increased over the years (Carslaw 2005, Minoura and Ito 2010). This is a result of NO₂ being introduced into the environment directly from diesel vehicle emissions and increasing ozone concentrations, in turn

increasing the percentage of NO undergoing oxidation to NO₂. Furthermore, the ratios of NO₂/NO_x near roadways are constantly changing influenced by several other factors, including season, traffic speed, amount of ozone present, and distance from source (Carslaw 2005, Minoura and Ito 2010). Therefore, the ratio of NO₂/NO_x can range from 0.05 to 0.35 and total NO_x concentrations as high as 200 ppb and 180 ppb were measured in London and Tokyo, respectively (Carslaw 2005, Minoura and Ito 2010).

Numerous studies have shown that short-term NO_x concentrations can have negative impacts on human health. The hypothesis that traffic-related pollution is associated with respiratory symptoms has been supported by research in Europe and the US (Kim et al. 2004; McConnell et al. 2010). From these studies, it is suggested that NO₂ may be an etiologic agent, causing both asthma and bronchitis in children (Kim et al. 2004). As a result, the EPA has initiated new goals to limit short-term exposure of NO₂ common to near roadway microenvironments. Because roadway microenvironments are not currently monitored, it is unclear how many areas will be declared un-attainment areas. Thus, most are designated as “unclassified.” In 2013, monitoring of short-term concentrations near major roadways in urban areas will be required (EPA 2010).

Several methods have been investigated to reduce vehicle emissions, such as lean NO_x traps and Selective Catalytic Reduction (SCR). However, drawbacks exist with both techniques, such as the potential for producing secondary pollutants and thermal durability. An alternative solution is heterogeneous photocatalysis, in which a semiconductor activated by light at a particular wavelength creates hydroxyl radicals, (*OH) and superoxides (O₂⁻) that accelerate the natural decomposition process of organic pollutants (Fujishima et al. 2000). In contrast to other methods, pollutants are decomposed to nonhazardous waste products with little energy

requirements and little selectivity (Zhao and Yang 2003). A proposed mode of oxidation of nitrogen oxides via hydroxyl radical intermediates in the presence of this photocatalyst is presented in Figure 4.1.

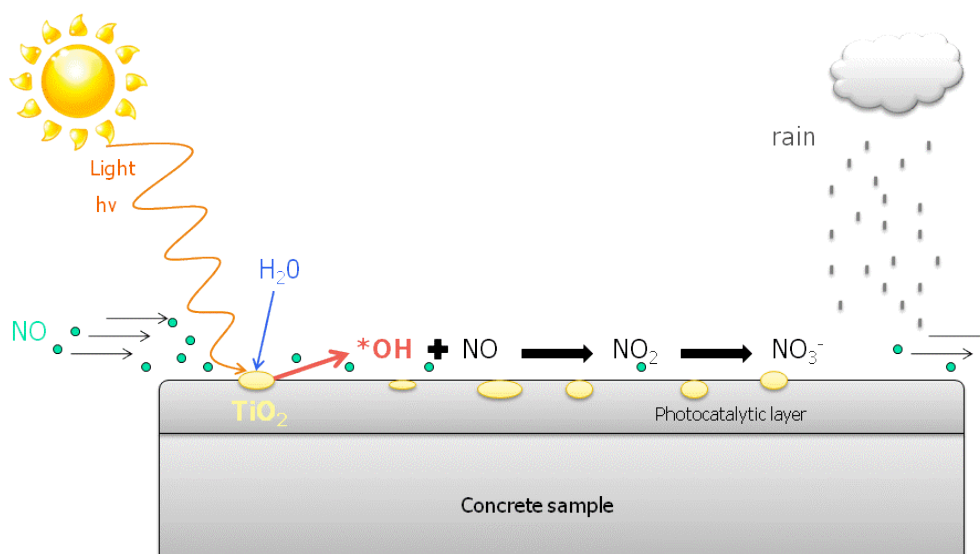


Figure 4.1 Illustration of the photocatalytic process

Various studies have incorporated photocatalytic oxidation in building materials for NO_x reduction. Beelden (2008) studied photocatalytic concrete blocks' ability to decompose NO_x pollutants. The concrete blocks consisted of an upper cement coat containing TiO_2 . Poon and Cheung (2007) incorporated TiO_2 into several different concrete surface mix designs by changing the aggregates design. Hassan et al. (2010) evaluated three methods of application for TiO_2 to concrete pavement, a cementitious-based ultra-thin coating, a water-based titanium dioxide solution, and sprinkling TiO_2 to the fresh concrete surface before hardening. The environmental benefits of applying an ultra-thin TiO_2 coating or a water-based TiO_2 solution were greater than the sprinkling method.

Although photocatalytic oxidation was proven effective in reducing NO_x emissions, the impact of NO_2 pollution and its effects on overall NO_x reduction efficiencies have not been

evaluated. Since NO_2 is a highly unstable gas, it is more difficult to study. For example, reactions such as heterogeneous hydrolysis of NO_2 convert NO_2 into HNO_3 if water is available on the surface. This reaction has been noted to occur on many urban surfaces, including concrete (Ramazan et al. 2004). Meanwhile, other studies described losses of NO_x due to alkaline oxides forming in the cement matrix, which aids in NO_x adsorption and would be an added benefit to use cement as a substrate for heterogeneous photodegradation (Cassar et al. 2003).

4.3 Experimental Program

The objective of the experimental program was to evaluate the effects of different NO_2/NO_x ratios on the effectiveness of photocatalytic concrete pavement to purify the air from NO_x gases. For this purpose, five different factors were tested: NO_2/NO_x ratio, concentration of TiO_2 , mix design, humidity level, and flow rate. The test setup used to quantify NO_x removal efficiency was modified from the Japanese Industrial Standard (JIS TR Z 0018 “Photocatalytic materials – air purification test procedure”) in order to accommodate larger samples (JIS 2009). This setup included a photocatalytic testing device, referred to as a photoreactor, which creates an enclosed controlled environment where the UV lights and the atmosphere can be simulated. The setup consists of a pollutant source (gas cylinder of NO), zero air source, adjustable valves, humidifier, calibrator, photoreactor, and chemiluminescent NO_x analyzer, see Figure 4.2.

4.3.1 Photoreactor

The structure of the photoreactor is made of plywood, to make it more cost effective and easier to manufacture. All the surfaces in contact with the gas were covered with Teflon coating. The connection between the outside Teflon tubing and the chamber was made with 316 stainless-steel funnels (inlet and outlet), Teflon tube and fittings. These materials have been used to ensure gas

compatibility, and are approved materials according to EPA and the Japanese Industrial Standard.

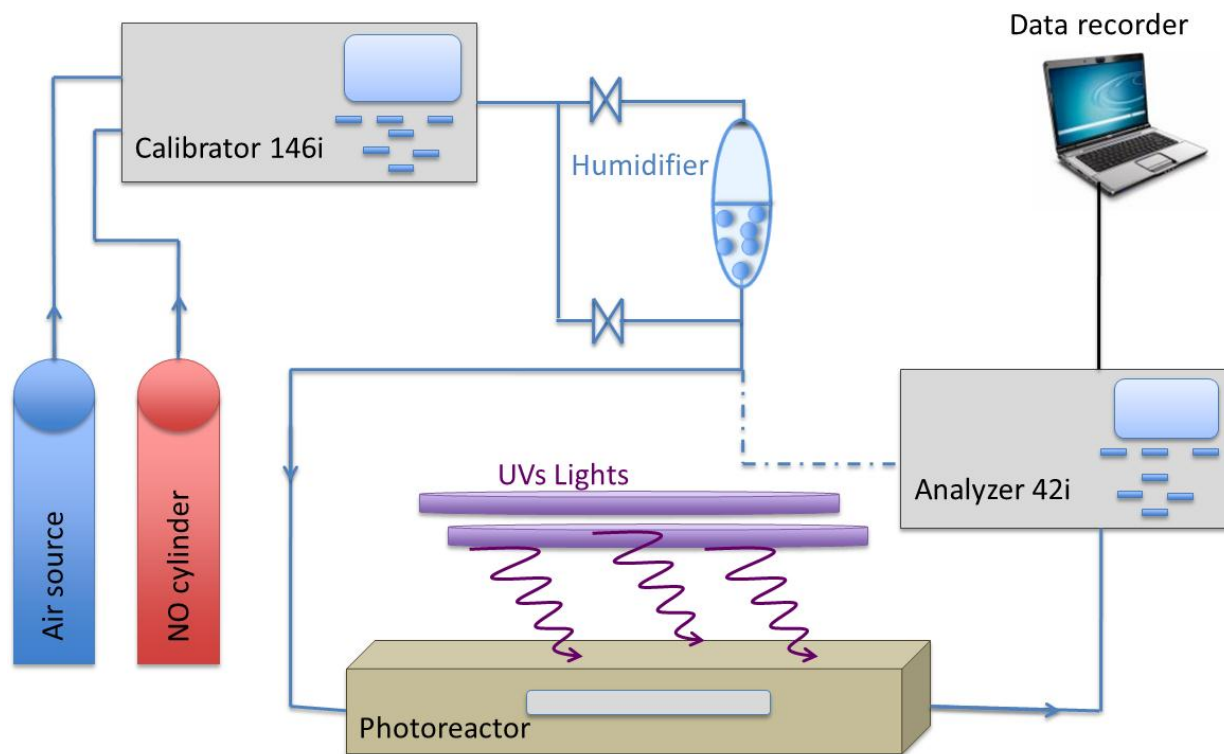


Figure 4.2 Experimental Setup Flow Diagram

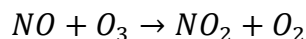
To fit with the sample sizes (305 mm x 380 mm x 50 mm), the dimensions of the chamber were enlarged. The external dimensions are 410 mm x 1170 mm x 140 mm. As recommended by the JIS standards in order to ensure a laminar flow, the length of the chamber was calculated so that it represents about three times the sample length. The photoreactor was sealed shut by 316 stainless steel nut wings to keep a controlled environment inside. A hygro-thermometer sensor is inside the chamber to monitor the environmental conditions throughout the experiment. Experimental averages, minimum and maximums are recorded for each test run.

Unless otherwise noted, all tests were conducted at room temperature (22 +/- 2°C) with the relative humidity fixed at 20% (+/- 5%).

The glass used was made of borosilicate to ensure efficient transmission of the UV rays. UV light was used to imitate natural sunlight radiation required for the photocatalytic reaction. The UV lights are attached to the photocatalytic device, outside of the photoreactor so that the temperature does not increase inside the chamber. The UV light source is two 20W fluorescent lights mounted in parallel above the glass. The distance between the glass and the UV lights was 400 mm, and can be adjusted to vary the intensity. For the purpose of this experiment, the average UV light intensity at the concrete surface was kept constant at 2 mW/cm⁻² measured by a UV-A intensity meter OAI Model 306 at 365 nm.

4.3.2 Gas Supply and Analysis

The calibrator required a pollutant source and a clean air source. A Thermo 146i Gas Calibrator supplied a constant polluted air stream at a controlled flow rate. The Thermo 146i included the Gas Phase Titration (GPT) option. This option allows NO₂ to be created in a reaction chamber, using the rapid gas phase reaction between NO and O₃, based on the following chemical reaction:



The amount of NO₂ created can be changed by varying the amount of ozone created by adjusting the drive level of the ozonator in percentage when in the GPT mode (Thermo Scientific 2008). The amount of NO₂ created was measured by the Thermo 42i NO_x analyzer, which was also used to measure NO_x removal efficiency. The resulting GPT percentages used to simulate NO₂/NO_x ratios of 0.70, 0.45, 0.2, and 0 were 25%, 20%, 15%, and 0, respectively. These ratios were all determined at a NO concentration of 550 ppb and a flow rate of 3 l/min.

To quantify the effectiveness of the photocatalytic concrete layer under different operating conditions, the JIS standard was used. The procedure calls for each sample to be tested for a total time of five hours under UV-irradiation, that is, started after at least 30 minutes to ensure equilibrium concentrations. The environmental efficiency is calculated by analyzing the concentrations of NO, NO₂, and NO_x with the “lights on,” compared to the difference in concentrations with the equilibrium at “lights off.” Figure 4.3 illustrates the typical variation of NO_x concentration during the testing process.

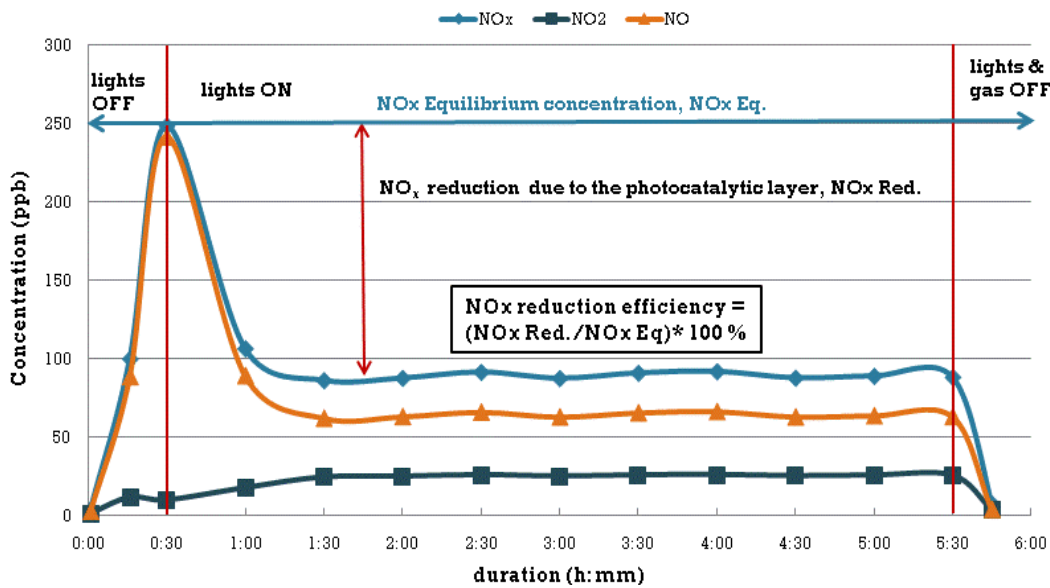


Figure 4.3 Variation of NO_x concentration during the experiment

4.3.3 Experimental Design

A partial factorial design was conducted for four of the five factors at a constant relative humidity of 20% to provide an indication of the influence of each factor on the photocatalytic effectiveness. Two levels (low [-] and high [+]) were considered for each factor, as shown in Table 4.1. The resulting total number of runs required is calculated from the definition of the factorial design, $2^{(k-p)}$; where k is the number of factors and p is one, representing the half fraction. There are eight combinations with three replicates to account for variability. The

resulting eight combinations for the experimental design are shown in Table 4.2. Further investigation was conducted on the relative humidity, flow, and NO₂/NO_x ratios. The additional levels tested are shown in Table 4.1.

Table 4.1 Test factorial for the NO₂/NO_x experiment

Variables	Factor	Low Level	High Level	Additional Levels
(1)	(2)	(-) (3)	(+) (4)	Tested (5)
Percentage of TiO ₂	1	3%	5%	-
Aggregate Gradation	2	No Fines	With Fines	-
NO ₂ /NO _x ratio	3	0	0.45	0, 0.2, 0.45, and 0.70
Flow Rate (l/min)	4	3	8	1, 3, 8
Humidity Level (%)	-	-	-	15, 25, 35, 50, and 80

Table 4.2 Factorial Experimental Design

Combination	1	2	3	4
(1)	(2)	(3)	(4)	(5)
1	-	-	-	+
2	+	-	-	-
3	-	+	-	-
4	+	+	-	+
5	-	-	+	-
6	+	-	+	+
7	-	+	+	+
8	+	+	+	-

4.3.4 Laboratory Samples and Materials Tested

Prepared samples consisted of a concrete base and a photocatalytic TiO₂ surface coating. The base was made of a concrete mix design, typically used in Louisiana in order to achieve a compressive strength of 41 MPa. The concrete base layers were cast in a wood mold of 310 mm x 381 mm x 40 mm. A second, removable layer was attached to the mold for the pouring of the photocatalytic concrete layer of 10 mm (Figure 4.4). The photocatalysis surface coating was applied after the concrete initial setting. The photocatalytic coating consisted of ultrafine titanium dioxide, cement, aggregate filler, and water. The titanium dioxide nanomaterial used

was a commercially available *Cristal Millennium* PC105. The selected filler was sand with a maximum nominal size of 1.18 mm. The test matrix consisted of four different surface mix designs, two different TiO₂ contents, and two different aggregate gradations (with fines and without fines). The surface mixes produced with no fines were prepared by removing all fines 300 µm or smaller from the sand filler. The surface mixture was prepared at a water-cement ratio of 0.6. Three replicates were produced of each test condition to account for variability.

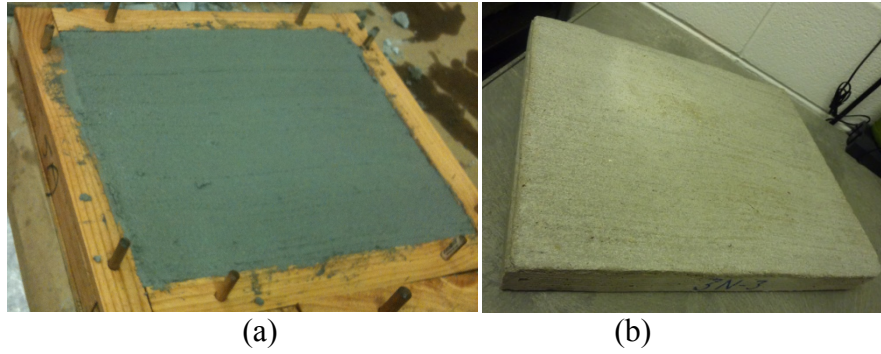


Figure 4.4 (a) Concrete Base Layer and (b) Finished Sample with the Photocatalytic Coating

4.4 Results and Analysis

The influence of operational and design factors (TiO₂ content, aggregate gradation, NO₂/NO_x ratio, and flow rate) on the NO_x removal efficiency was quantified. The effect of a given factor was determined, based on the following equation:

$$e_f = \frac{\sum_{i=1}^n \pm f_i R_i}{4} \quad (1)$$

where e_f = effect of factor $f=1, 2, 3$, or 4 ; n = number of experimental design run $n = 8$, R = NO_x reduction efficiency per run; and \pm : sign used to describe low and high levels for each factor. The effect of each factor is shown in Table 4.3. It is evident from the near zero main effects calculated, e_1 for the titanium content and e_2 for the aggregate design, that the mix design factors had little impact on NO_x removal efficiency. In contrast, the main effects, e_3 and e_4 ,

representing the ratio of NO_2/NO_x and the flow rate respectively, indicate that there was a decrease in efficiencies with higher NO_2/NO_x ratios and higher flow rates. Furthermore, the flow rate had a larger average negative impact on the NO_x reduction efficiencies, compared to the NO_2/NO_x ratio. As a result, further analysis was conducted to better understand the relationship between the NO_2/NO_x ratio and flow impacts on the NO_x reduction efficiency. Results of this analysis are presented in the following sections.

Table 4.3 Main effects of operational and design factors

Factor (1)	Effect (2)	Rank ¹ (3)
TiO ₂ Content	-0.08	4
Aggregate Gradation	1.2	3
NO_2/NO_x Ratio	-5.0	2
Flow Rate	-8.8	1

¹: rank of the influence on NO_x reduction efficiency

4.4.1 NO_2/NO_x Detailed Analysis

As it was previously mentioned, an increase in NO_2/NO_x ratio results in a decrease in NO_x reduction efficiencies. To further understand this trend, the NO_x removal efficiency was measured at four different NO_2/NO_x ratios (see Table 4.1). In this part of the experiment, the flow rate was kept constant at 3 l/min and the relative humidity at 20% ($\pm 5\%$). Under these conditions, the average reduction was as high as 75% when no NO_2 was present and as low as 42% with 70% NO_2 (see Figure 4.5). As expected from the main effect results, the NO_x reduction efficiencies did not change substantially between the four mix designs. Meanwhile, it is clear from Figure 4.3 that as the ratio of NO_2/NO_x increases, the overall NO_x reduction efficiencies decrease. When increasing the NO_2/NO_x ratio from 0 to 70%, the NO_x reduction efficiencies dropped 32%, representing 56% of the total efficiency.

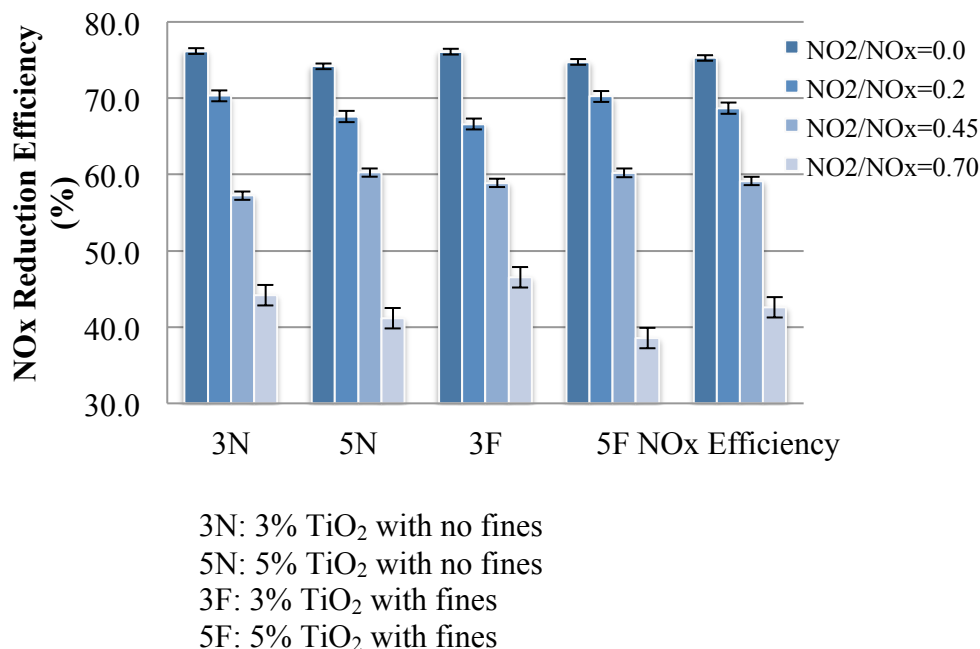


Figure 4.5 Impact of NO₂/NO_x ratio on NO_x reduction efficiency

One may hypothesize that the reduction in NO_x removal efficiencies is the result of the increase in the NO₂/NO_x ratio. However, as the NO₂/NO_x ratio increased, the initial equilibrium concentration of the NO_x also decreased, as shown in Figure 4.6. The lower initial concentrations are a consequence of the instability of NO₂. One explanation of the loss of NO₂ is through a reaction between NO₂ and the surface of the concrete sample, such as heterogeneous hydrolysis. To verify that the initial concentration was not a factor in the decreasing NO_x reduction efficiencies, the initial concentration was lowered while the ratio was kept constant. This was tested for two different NO₂/NO_x ratios, one without NO₂ and one with 20% NO₂ under the same test conditions. Figure 4.7 reveals that the NO_x reduction efficiencies remained mostly constant, regardless of the initial pollutant concentration.

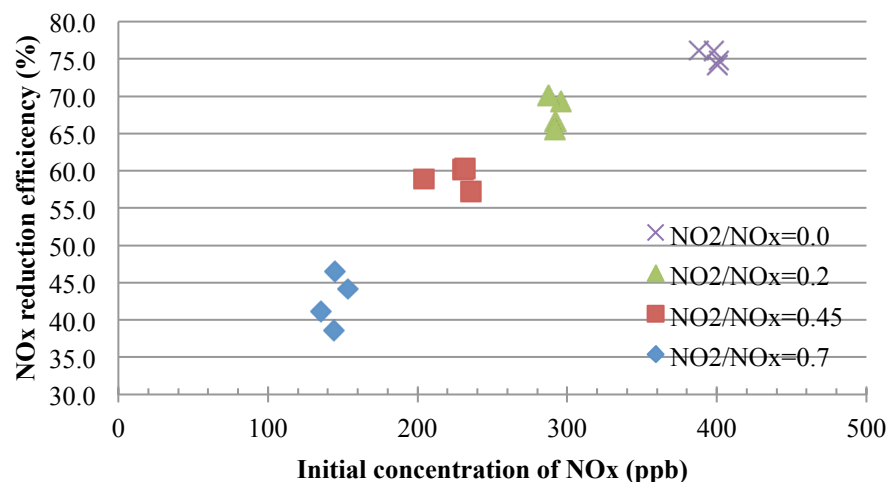


Figure 4.6 Impact of initial concentration on the NO_x reduction efficiency at various NO₂/NO_x ratios

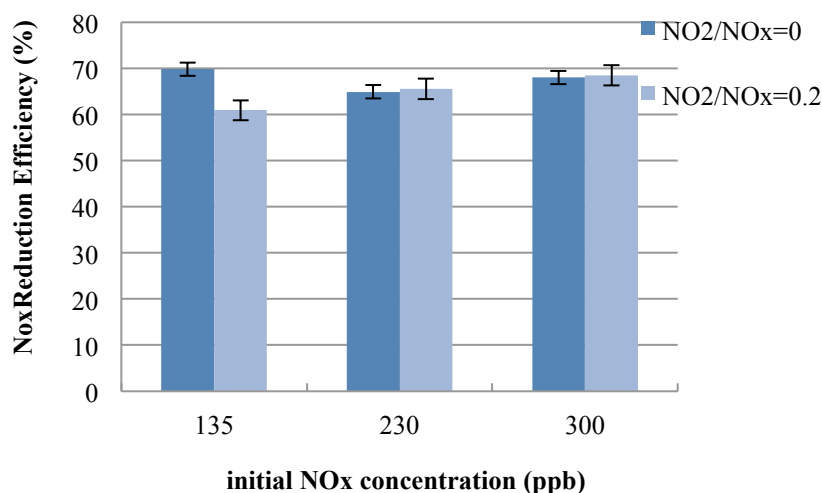


Figure 4.7 Impact of the initial concentration on the NO_x reduction efficiency

4.4.2 Flow Detailed Analysis

As previously mentioned, the flow rate had a significant impact on NO_x reduction efficiencies. With faster flow rates, there is less contact time for a reaction to occur, which results in lower reduction efficiencies. To evaluate this trend when NO₂ is introduced, the flow was varied from 1, 3, and 8 l/min at four different NO₂/NO_x ratios. Figure 4.8 shows the relationship between flow rates, NO₂/NO_x, ratio and NO_x reduction efficiency. As shown in this figure, the increase in

flow rates and NO_2/NO_x ratios resulted in a decrease in NO_x reduction efficiency. It is important to emphasize that the equilibrium concentrations changed when the flow rate changed. The amount of NO_2 reduced from the equilibrium concentration was greater at slower flow rates. In fact, when the inlet stream was completely NO_2 , the majority of the NO_2 was scrubbed at the concrete surface without photocatalytic degradation. For this reason, no NO_x photocatalytic reduction was observed and this point has been omitted in Figure 4.8. This further supports the theory of a reaction such as heterogeneous hydrolysis taking place between the unstable NO_2 and the concrete surface.

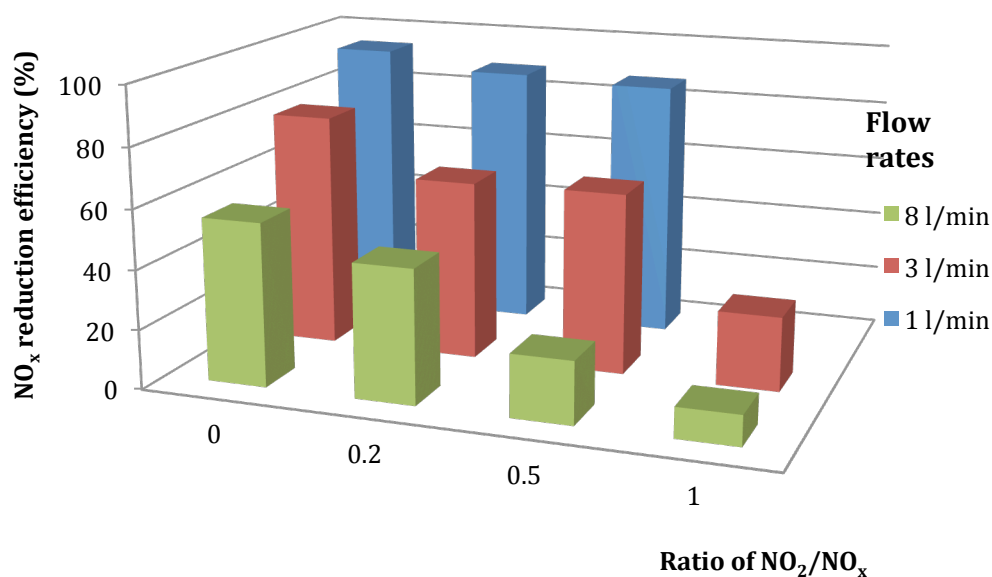


Figure 4.8 Effect of flow rate on the NO_x reduction efficiency at various NO_2/NO_x ratios

4.4.3 Effect of Relative Humidity

The impact of relative humidity on NO_x reduction efficiency was investigated. Figure 4.9 illustrates the variation of NO_x reduction efficiency with the relative humidity. As shown in this figure, humidity can have both a negative and positive impact on NO_x reduction efficiency, where the optimum relative humidity is near 25%. At relative humidity lower than 25%

humidity, the lack of water molecules required for the hydroxyl radicals hinders the photocatalytic oxidation. At higher relative humidity, the water molecules interfere with NO_x contact to the TiO_2 active sites on the surface (Dylla et al 2010).

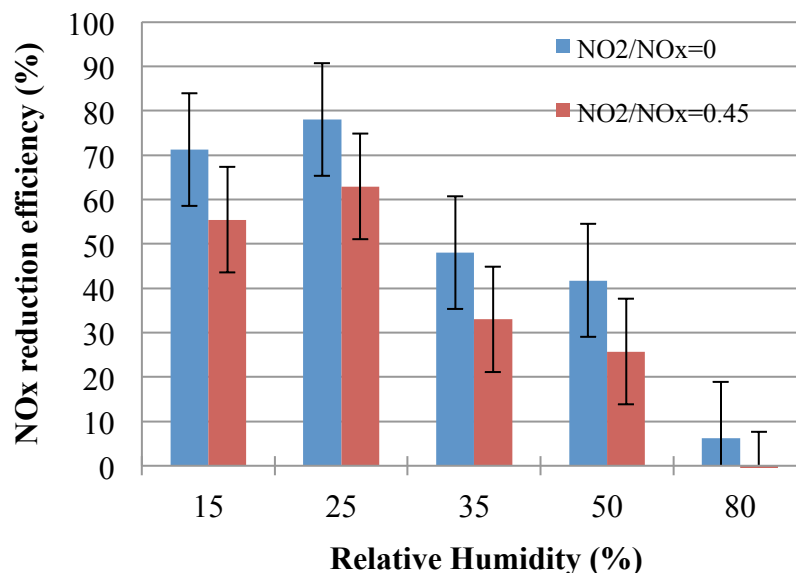


Figure 4.9 Effect of relative humidity on the NO_x reduction efficiency for different ratios of NO_2/NO_x

4.5 Conclusions

Nitrogen dioxide (NO_2) is a highly reactive gas that is usually not considered in the evaluation of TiO_2 photocatalytic activities. The unstableness of NO_2 is exhibited in the increasing variability in NO_x reduction efficiencies as more NO_2 is introduced. The objective of this study was to evaluate the impact of NO_2 in the photocatalytic process of NO_x . Based on the results of the experimental program, it is determined that the NO_2/NO_x ratio has a significant impact on NO_x reduction efficiencies; however, the extent of this impact relies on many other factors, such as flow rate.

The highest photodegradation rate was observed at 25% relative humidity, which balances the availability of hydroxyl radicals at the surface with NO_x contact with the

photocatalytic surface. Results of the experimental program showed that increasing the flow rate and NO_2/NO_x ratio negatively affect the effectiveness of the NO_x reduction efficiency. This is a result of most of the NO_2 being scrubbed through reaction with the concrete surface. However, within the evaluated range, the titanium content and aggregate gradation had little impact on NO_x removal efficiency. Further research should be conducted to confirm the heterogeneous hydrolysis reaction occurring at the concrete surface.

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CHAPTER 5

EFFECTS OF ROADWAY CONTAMINANTS ON TITANIUM DIOXIDE PHOTODEGRADATION OF NO_x³

5.1 Introduction

There is an increasing awareness of the impacts of roadway air quality microenvironments on the public. Research suggests that initial air quality standards are not strict enough and are underestimating the potential chronic harms of highway air pollutants (Kunzli et al. 2003). Numerous studies have shown that even short-term high pollutant concentrations can have negative impacts on public health. For example, nitrogen oxides (NO_x) (traffic-related pollution) are associated with chronic respiratory symptoms and asthma (Kim et al. 2004, McConnell et al 2010). Moreover, NO_x is a precursor to more dangerous pollutants such as ground level ozone. High tropospheric ozone concentrations also have negative health impacts. Studies have shown a positive correlation between ozone concentration and increased risk of death from respiratory causes (Jerrett et al. 2009). As a result, stricter regulations specific to short-term pollutant concentrations near major roadways will be in effect, starting 2013 (EPA 2010^a).

Several counties within the US are classified as nonattainment areas for ground level ozone. Large metropolitan areas such as Los Angeles, CA, and Houston, TX, range from extreme to severe classifications for which vehicle emissions are largely responsible (EPA 2010^b). In 2000, this equated to approximately 25% of Americans living in ozone nonattainment areas and 4% of Americans in areas exceeding NO_x emissions standards (Kunzli et al. 2003). Several strategies exist to reduce roadway microenvironment pollution; however, many techniques will take time to implement and others have the potential of producing secondary

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pollutants. Even with recent advancements in engine technologies, the majority of vehicles sold in the US are not making use of these technologies. As a result, health officials are urging for faster and more implementable solutions to reduce the impacts of traffic emissions (Kunzli et al. 2003).

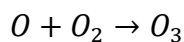
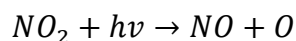
One promising solution is to utilize pavement roadways to remove pollutants from the environment by means of an effective photocatalytic layer such as titanium dioxide (TiO₂). Researchers have demonstrated that photocatalytic pavements can significantly remove organic pollutants such as NO_x and VOCs in the presence of sunlight without impacting pavement durability (Dylla et al. 2010). However, in order to ensure successful implementation of this technology, the potential impacts of operating conditions on the photocatalytic layer should be investigated. One particular impact that has not been evaluated is the efficiency of the photocatalytic reaction under various soilure conditions. Various contaminants may cover the photocatalytic layer interfering with its ability to be irradiated by the sunlight to decompose pollutants. Such common roadway contaminants include dirt, motor oil, and de-icing salts. Therefore, the objective of this study was to quantify the impact of common roadway contaminants on the effectiveness of photocatalytic roadways' ability to remove NO_x from the atmosphere.

5.2 Background

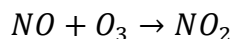
Nitrogen Oxide (NO_x) is a group of highly reactive gases, specifically nitric oxide (NO) and nitrogen dioxide (NO₂) formed from high temperature fuel combustion (EPA 2010^a). Many negative impacts are associated with NO_x emissions, such as formation of tropospheric ozone, urban smog, acid rain, and fine particle pollutions, which are associated with many adverse health effects (Jimenez et al. 1999). Although the US has few areas in violation of NO_x air

quality standards, it is unknown how many road microenvironments will be in violation of the new 2013 standards. Furthermore, a major concern is NO_x contribution to ground level ozone in which many counties are still in violation.

Ground level ozone is formed in the air from NO_x emissions through photolysis shown by the following sequences when exposed to sun and heat, where $h\nu$ is the energy of light calculated by, h , Planck's constant multiplied by ν , the frequency of light (Atkinson et al. 2000, EPA 2010°):



Conversely, ozone is consumed in the reaction creating NO₂ usually ending in no net change in ozone:



However, when volatile organic compounds (VOC's) are introduced, also released from vehicle emissions, radicals in the air convert additional NO to NO₂ and thus contribute to an ultimate net gain of ozone (Atkinson et al. 2000, Sillman 1999). These reactions are accelerated by sunlight and heat resulting in higher ozone concentrations during the day and away from the pollutants' source (Beckerman et al. 2008, Jo and Park 2005). This cycle indicates that reducing NO in the atmosphere will in turn reduce ground level ozone.

Photocatalytic compounds applied to the pavement surface have the benefits to be in close contact with vehicle emissions, as well as to be naturally more effective during times when

pollutants tend to be higher (i.e., during daylight). For this reason, several studies have suggested the incorporation of photocatalytic compounds in highway construction materials (Hassan et al. 2010, Beeldens, Chen and Li 2007). Three main application techniques have been suggested for concrete pavements: (1) apply a cementitious-based ultra-thin layer, (2) spray a water-based titanium dioxide solution, and (3) sprinkle TiO_2 to the fresh concrete surface before hardening (Dylla et al. 2010, Hassan et al. 2010). Comparison of the three application methods for concrete pavement has shown benefits and drawbacks for each application method (Dylla et al. 2010, Hassan et al. 2010). Past research showed that the environmental benefits of spraying a water-based TiO_2 solution are higher, because a higher concentration of TiO_2 is irradiated; however, the durability of the layer has not been evaluated in the field. For this reason, TiO_2 incorporated into a cementitious ultra-thin surface layer seems more durable while maintaining high environmental efficiencies before and after abrasion and wear (Hassan et al. 2010).

The photocatalytic efficiency depends on several factors and operating conditions, which result in a level of complexity in investigating the efficacy of photocatalytic materials (Huskens et al. 2009). For example, water vapor has both negative and positive impacts. The absence of water may hinder the reaction rates, as it is required to form the hydroxyl radicals that aid the accelerated degradation; whereas, too much water may create competition with the pollutant molecules absorbed (Dylla et al. 2010, Huskens et al. 2011). Furthermore, the removal efficiency is a function of the pollutants' flow rate. Amongst research, flow rates widely vary from 1 l/min to 8 l/min (Schmitt et al. 2011, Huskens et al. 2009). At slower flow rates, there is a longer period of gas residence time (the average amount of time that a pollutant spends in the system), which correlates to increased removal efficiencies. As the flow rate decreases, shorter residence periods equate to lower efficiencies (Dylla et al. 2010). Additional parameters that

have not been investigated are various soilures and contaminants that may interfere with the photocatalytic reaction (Yu 2002).

5.3 Experimental Program

The objective of the experimental program was to evaluate the effects of three common road soilures, i.e.) dirt, de-icing salt, and oil, on the photocatalytic degradation of NO_x . To achieve this objective, a mix design for the photocatalytic layer, which was successfully evaluated in a previous study, was adopted (Hassan et al. 2010). The mix design for the photocatalytic layer consisted of ultrafine titanium dioxide (Cristal Millennium PC105), cement, filler, and water. The selected filler was sand with a maximum nominal size of 1.18 mm. The effects of relative humidity, contaminant coverage level, and flow rate were investigated. The TiO_2 content was kept constant at 3% of the weight of cement, based on the results of previous studies (Hassan et al. 2010). The surface mixture was prepared at a water-cement ratio of 0.6.

Two levels (low [-] and high [+]) were considered for each factor, as shown in Table 5.1. The resulting total number of runs required is calculated from the definition of the factorial design, $2^{(k)}$; where k is the number of factors such that there are eight combinations with three replicates to account for variability (i.e., $k = 3$). The resulting eight combinations for the experimental design are shown in Table 5.2. The averages of the three replicates were used to calculate the main effects for the considered factors, which provided an indication of the influence of each factor on the photocatalytic effectiveness. For comparison purposes, a control run of three replicates was tested without any soiling at the low relative humidity and low flow rate levels (i.e., 20% humidity and 3 l/min flow rate).

Table 5.1 Factorial Experimental Design Factors

Factor	Factor number	Low (-)	High (+)
Salt level (gram)	1	None	30.0
Dirt level (gram)		None	12.0
Oil level (gram)		None	6.0
Relative humidity (%)	2	20	80
Flow rate (l/min)	3	3.0	8.0

Table 5.2 Factorial Experimental Design

Combination	1	2	3
1	-	-	-
2	+	-	-
3	-	+	-
4	+	+	-
5	-	-	+
6	+	-	+
7	-	+	+
8	+	+	+

Before switching the soilure type, each concrete sample was regenerated and retested to ensure the same initial photocatalytic capacity. The samples were regenerated following the Japanese standard JIS TR Z 0018 “Photocatalytic materials – air purification test procedure” (JIS). The procedure consisted of two immersions in clean water for an hour each. After regeneration, the samples were dried for 48 hours in a temperate room before being retested, at the initial conditions (3 l/min inlet pollutant flow rate corresponding to a 7 minute gas residence time and 20% of relative humidity) without any spoilage to the photocatalytic coating to ensure initial capability.

5.3.1 Laboratory Samples and Materials Tested

Each sample consisted of two layers, the base, prepared with a concrete mix design widely used in Louisiana that would achieve a compressive strength of 41 MPa and the photocatalytic concrete surface coating, which was applied using a method successfully evaluated in previous

studies (Hassan et al. 2010). The concrete base layer was poured in a wood mold of 310 mm x 381 mm x 40 mm; a second removable form was then attached to the mold in order to pour the photocatalytic layer of 10 mm (Figure 5.1). The photocatalytic layer was poured approximately one hour after the concrete base.

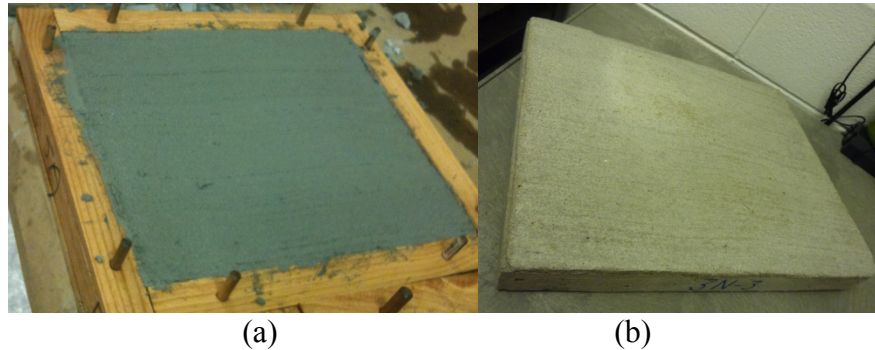


Figure 5.1 (a) Concrete Base Layer and (b) Finished Sample with the Photocatalytic Coating

5.3.2 Sample Soilure

The amount of coverage was determined by the weight of substance added, with Level 1 consisting of half the contaminants added at Level 2. Level 2 corresponds to the high level factor in the factorial experimental design, which was compared to the low factor, being the control samples with no soilure. In order to simulate dusty conditions, a silty-clay type soil was uniformly applied to the sample surface. The selected oil was a commercially available motor oil (10W-30). The de-icing salt chosen was a commercially available primary sodium chloride rock. The visual aspect of every type of soiling at low and high coverage levels is shown on Figure 5.2 (a through f).

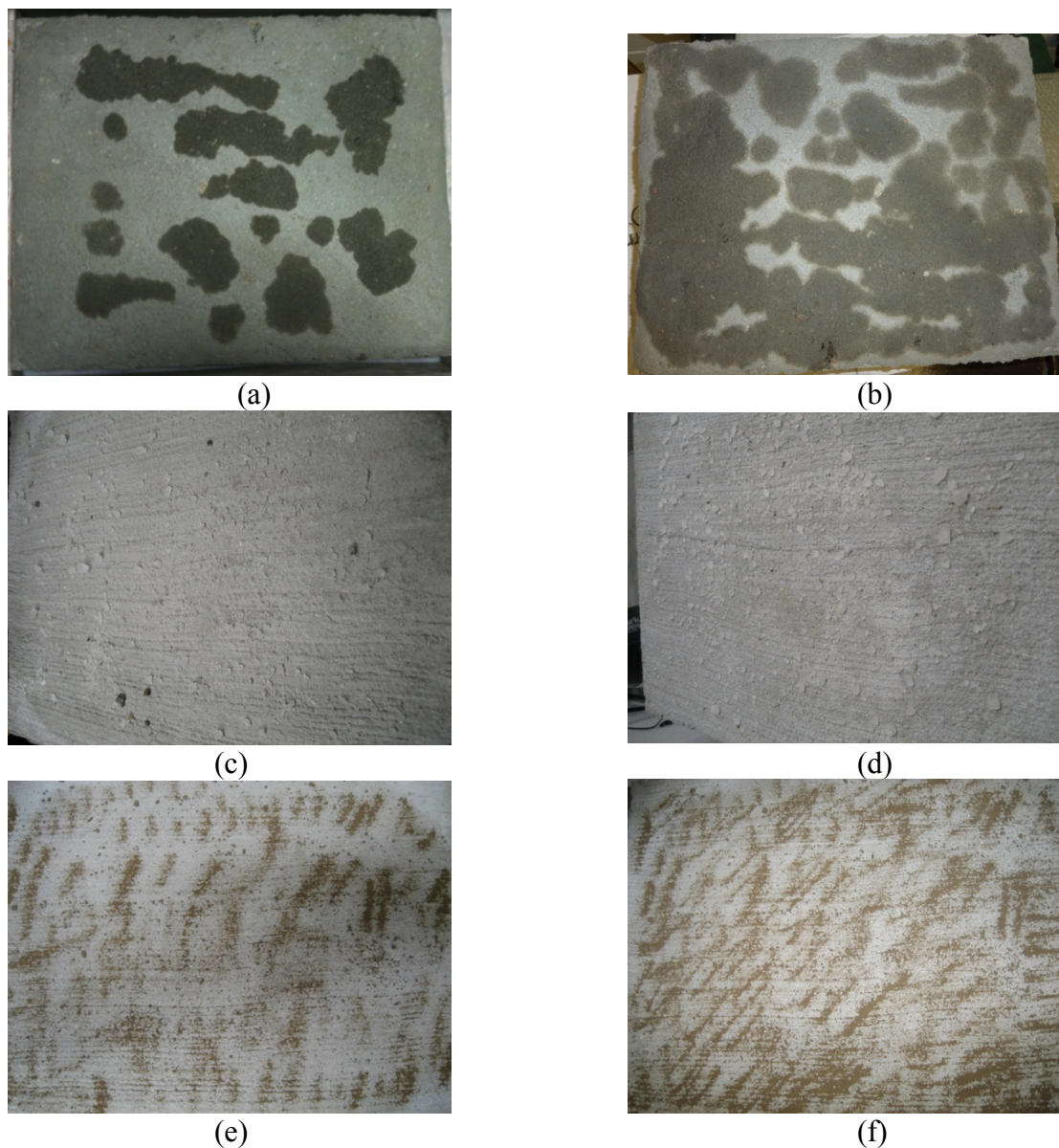


Figure 5.2 Contaminations of the Photocatalytic Surface at Low and High Levels of Coverage for Oil (a and b), De-icing Salt (c and d), and Dirt (e and f)

5.3.3 Environmental Test Setup

The environmental performance of the photocatalytic coating was quantified by measuring different concentrations of NO , NO_2 , and NO_x . The test setup used was modified from the JIS TR Z 0018 standard to accommodate larger samples (JIS 2004). This setup consists of a

pollutant source (gas cylinder of NO), zero air source, adjustable valves, humidifier, calibrator, photoreactor, and chemiluminescent NO_x analyzer, as shown in Figure 5.3.

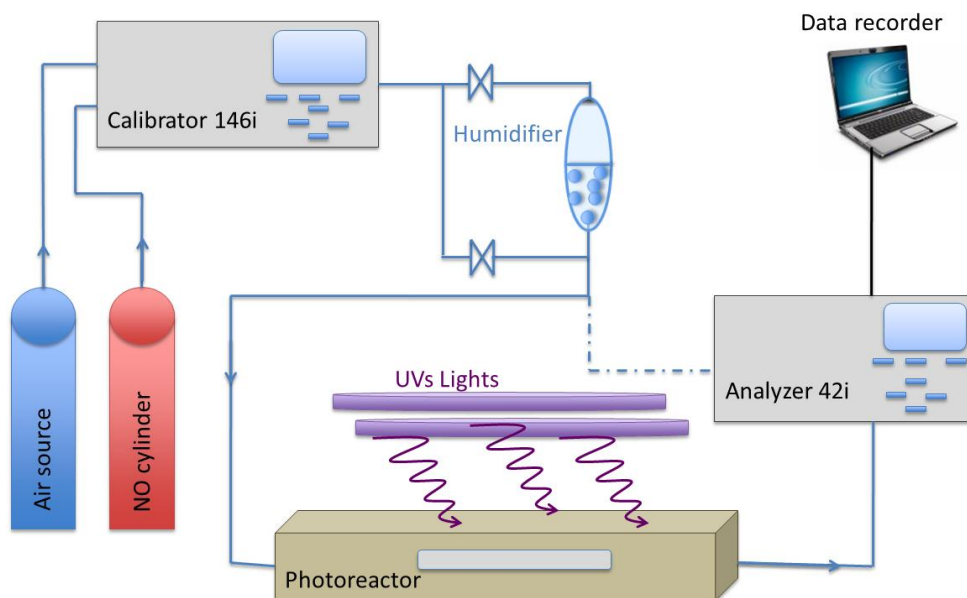


Figure 5.3 Experimental Setup Flow Diagram (Dylla 2011)

The calibrator, requiring a pollutant and zero air source, controls inlet flow and NO_x concentrations, introduced to the sample through the photoreactor. Before entering the photoreactor, the inlet jet stream can continue through the humidifier or bypass the humidifier to simulate various humidity levels. A tee-connection before the photoreactor is connected to the NO_x analyzer to verify the inlet NO_x concentrations. As a result, the jet stream enters the photoreactor flowing over the sample at a controlled humidity, flow, and NO_x concentration. The photoreactor maintains this controlled environment for the sample. All tests were conducted at room temperature of 24°C (+/- 2°C). UV lights are above the photoreactor to simulate UV lighting for the photocatalytic reaction to occur. Finally, the outlet jet stream of the photoreactor

is connected to the NO_x analyzer to measure any changes in pollutant concentration after being exposed to the sample.

5.4 Results and Analysis

To quantify the effectiveness of the photocatalytic concrete layer under different operating conditions, the Japanese standard JIS TR Z 0018 “Photocatalytic materials – air purification test procedure” was followed (JIS 2004). Figure 5.4 illustrates the variation of NO, NO₂, and NO_x concentrations during the course of the environmental experiment for the sample without contaminants. As NO_x concentration represents the summation of NO and NO₂ concentrations, Figure 5.4 shows that even though there is a slight increase in NO₂, the larger decrease in NO concentrations results in an overall decrease in NO_x concentrations. The JIS standard calls for each sample to be tested for a total time of five hours, during which UV-irradiation is started after an average of 30 minutes to ensure equilibrium concentrations. The time needed to reach equilibrium varies with the flow rate and the residence time. In general, it takes about 5 times the residence time for the NO_x concentrations to reach equilibrium. Hence, a 1 l/min flow rate corresponding to a 22 minute residence time requires 110 minutes; whereas, the 8 l/min flow rate corresponding to a 3 minute residence time requires 15 minutes to reach NO_x initial concentration equilibrium in the photoreactor. The environmental performance was calculated by analyzing the concentrations of NO, NO₂ and NO_x with the lights on, compared to the difference in concentration at the equilibrium concentration in the photoreactor with the lights off.

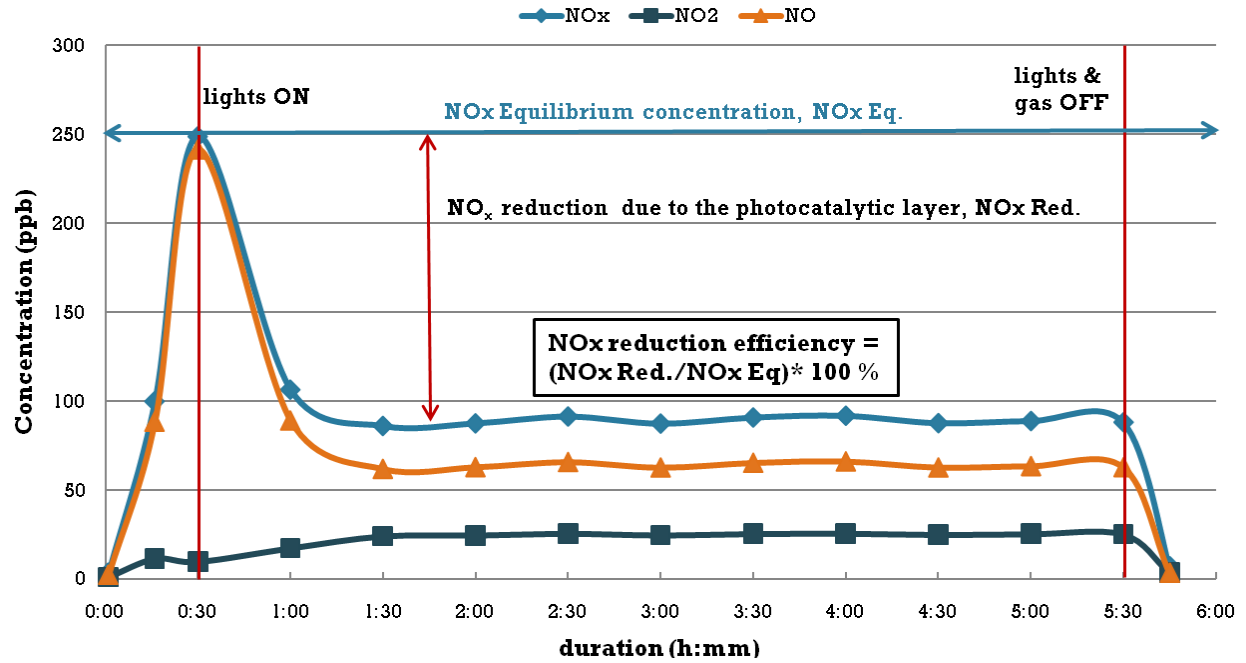


Figure 5.4 Variation of NO, NO₂, and NO_x Concentration during the Photocatalytic Experiment

5.4.1 Results of the Factorial Experimental Analysis

The influence of operational factors (contaminant level, flow rate, and humidity level) on the NO_x removal efficiency was quantified. The NO_x reduction efficiency for each test combination presented in Table 5.2 is shown in Table 5.3. The main effect quantifies the influence of each operational factor on the NO_x removal efficiency, based on the following equation (Law 2007):

$$e_f = \frac{\sum_{i=1}^n \pm_f R_i}{4} \quad (1)$$

where,

e_f = main effect for factor $f = 1, 2$, and 3 ;

n = number of experimental design runs ($n = 8$);

R = NO_x reduction efficiency for each run; and

±_f = sign used to describe low and high levels for each factor f = 1, 2, and 3.

Table 5.3 NO_x Reduction Efficiency for each Test Combination

Combination	Soiling Level	Humidity Level	Flow Rate	NO _x Reduction Efficiency (%)		
				Dirt	Salt	Oil
1	-	-	-	76.2	76.2	76.2
2	+	-	-	69.3	61.3	36.7
3	-	+	-	6.1	6.1	6.1
4	+	+	-	5.4	3.2	1.5
5	-	-	+	55	55	55
6	+	-	+	48.1	30.5	18
7	-	+	+	0	0	0
8	+	+	+	0	0	0

The calculated main effects for each operational factor are presented in Table 5.4. The main effect quantifies the influence of each factor (i.e., soiling type, relative humidity, and flow rate) on the NO_x removal efficiency based on Equation (1). The main effects (e_f) represent the average change in the NO_x removal efficiency, due to moving a given factor from its low level to its high level while holding all other factors fixed. It is evident from the negative results for the soiling effects (e_1) shown in Table 5.4, that all contaminants tested had a strong negative impact on the photocatalytic NO_x removal efficiency. The impact of contaminants' coverage is largely dependent on the soilure type, with oil having the largest negative impact. As expected, both increases in the flow rate and the relative humidity also resulted in lower efficiencies. However, on average, the flow rate had the lowest decrease in efficiencies with increasing flow rates. In fact, it seems that the flow rate impact was the same regardless of the soilure type.

Table 5.4 Main and Interaction Effects of Roadway Contaminants

Main Effect	Description	Dirt	Salt	Oil
e ₁	Main effect of soiling level	-14.6	-42.3	-81.2
e ₂	Main effect of humidity level	-59.3	-53.4	-44.6
e ₃	Main effect of flow rate level	-13.5	-15.3	-11.9
e ₁₂	Interaction between soiling level and humidity	3.26	9.11	18.0
e ₁₃	Interaction between soiling level and flow rate	0.19	-1.66	1.79
e ₂₃	Interaction between humidity and flow rate	7.71	10.7	8.06

These findings are supported by the combined effects (i.e., interaction), e_{13} , between soilure level and flow rate, which are all near zero, indicating little to no interaction between the flow rate and soilure level. In contrast, the negative impact caused by relative humidity is intensified by the soilure level and type. Oil had the greater negative impact and dirt had the least negative impact. In addition, the average decrease by humidity was larger than all other factors except for the case of oil, which was more significant. As a result, further analysis was conducted to better understand the relationship between the soilure type and its combined effects with relative humidity and flow rate on the NO_x reduction efficiency. Results of this analysis are presented in the following sections.

5.4.2 Effect of Soilure Type and Levels of Contamination

As previously noted, an increase in soilure coverage resulted in a decrease in NO_x reduction efficiencies for all soilure types. To understand this trend, the NO_x removal efficiency was measured at two different coverage levels for each soilure type (see Figure 5.5). During this part of the experiment, the flow rate was kept constant at 3 l/min and the relative humidity at 20% (\pm 5%). Under these test conditions, the average reduction was as high as 79% with no soilure, and as low as 37%, 61%, and 69% for high coverage of oil, salt, and dirt, respectively. Oil had the largest negative impact. This could be a result of the photocatalytic degradation of oil, rather

than the NO_x . Further research would be required to confirm this hypothesis and measure degradation efficiencies of the motor oil. It is also noted that the motor oil is fluid and covered more surface area than the other containments, as shown in Figure 5.2. The reduction of NO_x efficiencies for dusty conditions did not exhibit the same negative trend, which was well defined in the case of the salt and oil soiling (see Figure 5.5). A plausible explanation is the possible interaction between humidity and dirt. The photocatalytic reaction requires water to create hydroxyl radicals and superoxides, which drive the photocatalytic degradation of pollutants (Dylla 2010). At coverage 1, dirt covers photoactive adsorption reaction sites similar to the other soiling types thus decreasing the overall efficiencies. However, at higher levels of dirt, its absorption of the humidity may contribute an adequate amount of water increasing the photocatalytic reaction efficiency.

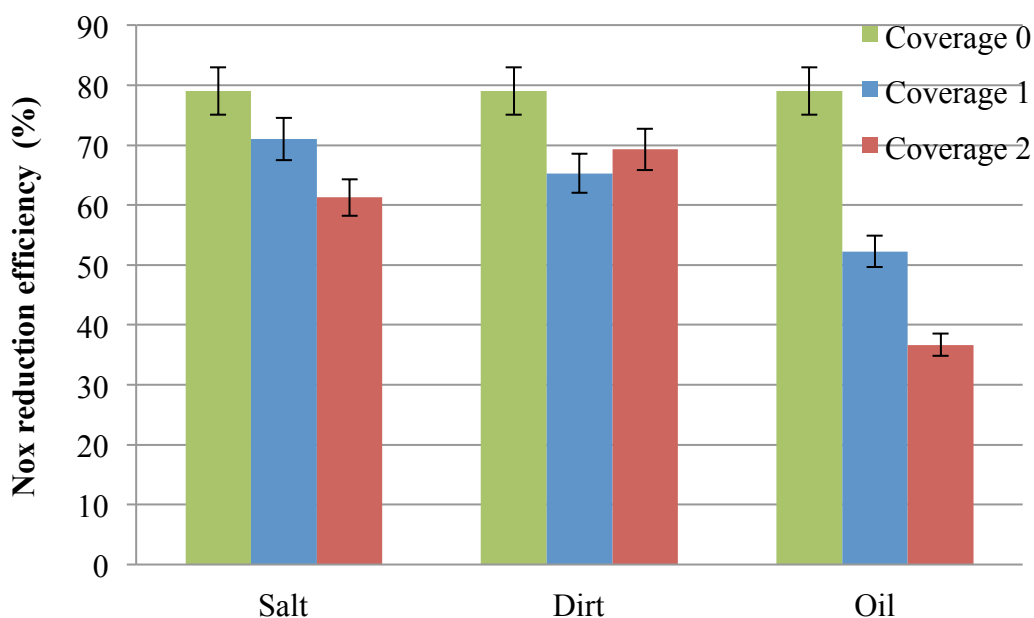


Figure 5.5 Effects of Soilure Type and Coverage Rate on NO_x Reduction Efficiency

5.4.3 Effect of Flow Rate

As it was previously noted, the increase in flow rate had a negative impact on NO_x reduction efficiencies. With faster flow rates, there is less contact time for the photocatalytic reaction to occur, which results in lower reduction efficiencies. To evaluate this trend when different soilure types are present, the flow rate was varied from 1, 3, and 8 l/min. During this part of the experiment, the soilure coverage was kept constant at the high level (Level 2) and the relative humidity at 20% ($\pm 5\%$). Figure 5.6 shows the relationship between flow rates, soilure type, and NO_x reduction efficiency. As shown in this figure, the increase in flow rates with the presence of soilure at the surface resulted in a decrease in NO_x reduction efficiency. Dirt is parallel to the control sample, thus the negative impact from dirt is most likely from inhibiting NO_x adsorption. The negative impact of salt on the NO_x reduction efficiency could be a result of a possible reaction occurring at the surface between salt, humidity, and air. The resulting products of this possible reaction could increase the competition of NO_x adsorption near photocatalytic active sites, thus decreasing the photocatalytic reduction of NO_x efficiency. It is noted that after regeneration of the salt runs, complete photocatalytic ability was recovered. Thus, if there was any reaction, the product was washed away and did not permanently inhibit the photocatalytic ability.

5.4.4 Effect of Relative Humidity

At a higher relative humidity, the water molecules interfere with NO_x contact to the TiO₂ active sites on the surface, and result in a decrease in NO_x reduction efficiency (Dylla 2010). To confirm this relationship when the surface is contaminated, the impact of relative humidity on NO_x reduction efficiency was investigated for each soilure type at three humidity levels, 20, 50, and 80% at 3 l/min constant flow. Figure 5.7 illustrates the variation of NO_x reduction efficiency

with relative humidity per soilure type. As shown in this figure, humidity had a negative impact on NO_x reduction efficiency. The dirt and the salt were the most impacted by the relative humidity. For the salt, this could be related to a reaction taking place between water and salt at the concrete surface. At high humidity levels, the salt reacted and created dark rings on the surface of the concrete, as shown in Figure 5.8. As for the dirt, this could be due to the dirt absorbing more water on the surface than normal concrete interfering with the reaction sites of the TiO₂, inhibiting degradation. However at high humidity, the impacts for each soilure type were similar, with all cases resulting in a NO_x reduction efficiency of 10% or less. Additional chemical analysis should be conducted to better understand the reaction that occurred with the salt and humidity at the concrete surface at a high humidity level.

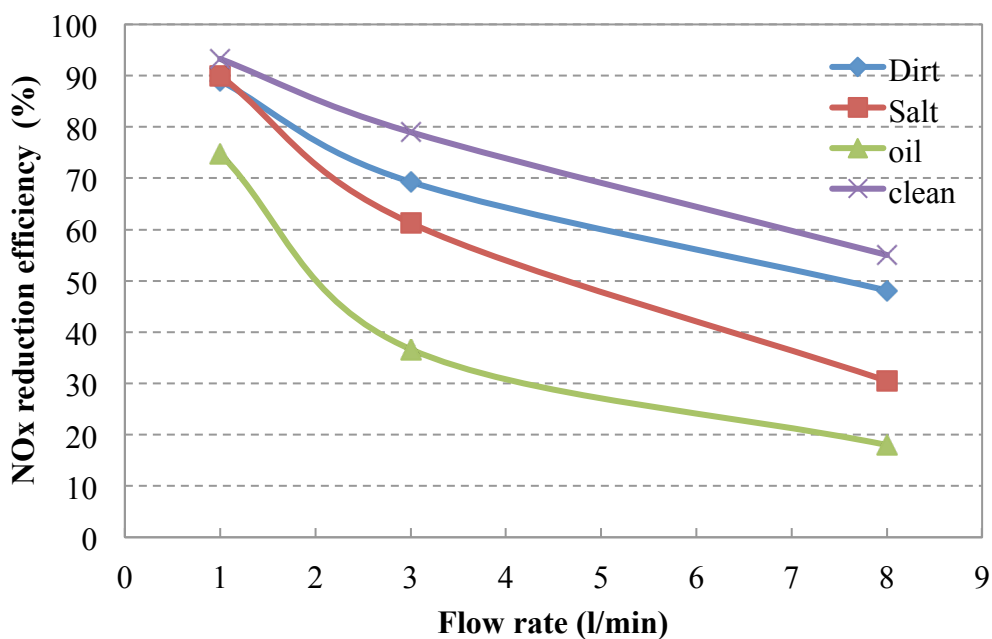


Figure 5.6 Impact of Flow Rate on the NO_x Reduction at 20% RH and Level 2 Contaminant Coverage

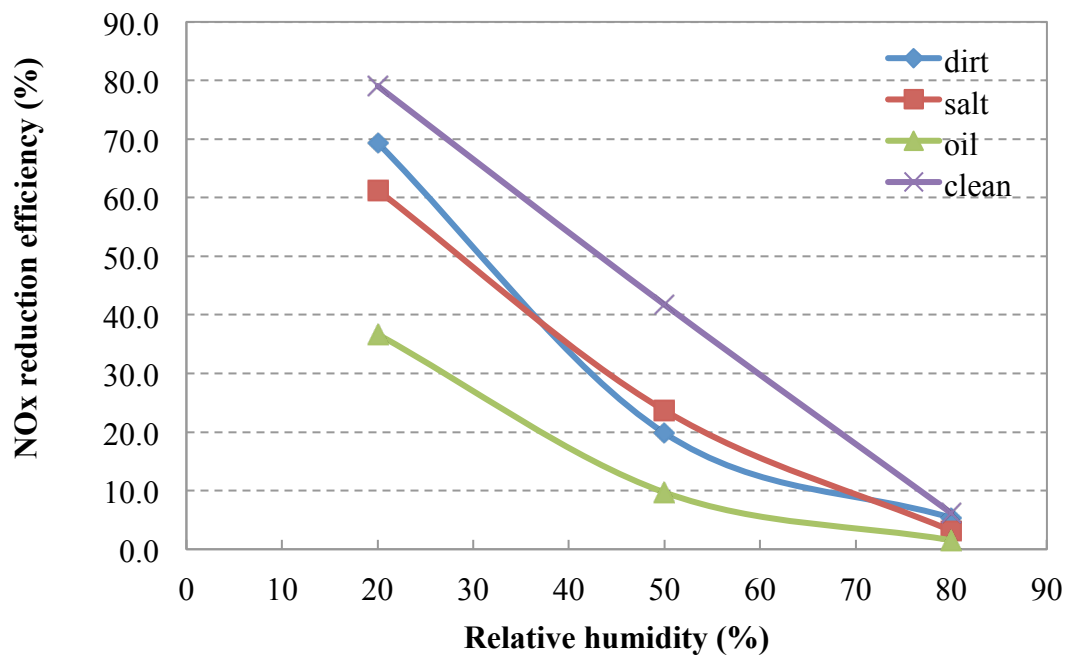


Figure 5.7 Impact of the Relative Humidity and Level 2 Contaminant Coverage on NO_x Reduction Efficiency



Figure 5.8 Reaction of Humidity at 80% with Salt at Level 2 Coverage

5.5 Conclusions

A photocatalytic compound such as TiO_2 is an effective method to reduce NO_x emissions and its negative impacts on human health. However, dirt, motor oil, and de-icing salts are three common roadway contaminants that may interfere with the photocatalytic layer. The objective of this study was to measure the impact of common roadway contaminants on the effectiveness of photocatalytic roadways' ability to remove NO_x from the atmosphere. Based on the results of the experimental program, the following conclusions may be drawn:

- The three contaminant types had a strong negative impact on the photocatalytic NO_x removal efficiency. The impact of contaminants' coverage was largely dependent on the soilure type with oil having the largest negative impact. The mechanism for the negative impact is most likely caused by competition for the adsorption areas. In addition, oil also competes with photocatalytic reactive sites; the larger negative impact could be a result of the photocatalytic degradation of oil, rather than the NO_x .
- An increase in the flow rate resulted in lower NO_x efficiencies. The increase in flow rates with the presence of contaminants at the surface resulted in a decrease in NO_x reduction efficiency. Although all soilure types exhibited similar decreasing trends, salt had the greatest impact on the flow rate. However, after regeneration of the salt runs, complete photocatalytic ability was recovered.
- An increase in the relative humidity had a negative impact on NO_x reduction efficiency. Dirt and salt were the most impacted by the relative humidity. For the salt, this could be related to a reaction taking place between water and salt at the concrete surface in which the resulting product increases the competition for adsorption area.

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CHAPTER 6

SUMMARY AND CONCLUSIONS

Self-cleaning, air-purifying concrete pavement is a rapidly emerging technology that can be constructed using air-cleaning agents with a super hydrophilic photocatalyst, such as titanium dioxide (TiO_2). Although this technology has the potential to support environmentally friendly road infrastructure, a number of design and operational parameters may affect its efficiency and must be evaluated. This study measured the NO_x reduction efficiencies from photocatalytic pavements under various environmental conditions common to photocatalytic highways. To achieve this, the project was split into three phases. The first phase of the project was to develop a photocatalytic concrete surface layer for air purification under known photocatalytic efficiency parameters of flow and humidity. The second phase was to evaluate the environmental effectiveness of TiO_2 photocatalytic pavements in photodegrading mixed NO_2 and NO gases from the atmosphere. The third and final phase was to evaluate the environmental effectiveness of photocatalytic concrete surface layers in photodegrading NO_x when exposed to common roadway contaminants.

In the first phase of the project, concrete photocatalytic samples were made using a two lift concrete system; a concrete base with a thin, photocatalytic, mortar overlay. The photocatalytic mortar mix was varied with two aggregate size distributions and two percentages of TiO_2 contents and its durability against repeated traffic loads, tested by the Hamburg loaded wheel tester. A new laboratory setup was designed to measure the photocatalytic reductions of NO_x specifically for pavement samples. Using this setup, the NO_x reduction of each mix was measured under known environmental parameters, including three levels of humidity and three levels of airflow.

Each mix design significantly reduced the NO and withstood the Hamburg loaded wheel test to ensure layer durability, due to cracking from repeated traffic loading. The mix design without fines achieved the highest photodegradation rates at the standard flow rate, however, at different flows, this trend changed. The increase from 3% to 5% TiO₂ resulted in little improvement in the NO removal efficiency; yet the cost-effectiveness of this improvement warrants justification. The NO removal efficiency decreased with the increase in humidity level. This may be because water inhibits absorption of NO by the photocatalytic compound, and thus hampers the photodegradation rates. As the flow rate increased, the percent NO removal efficiency decreased. This was expected; as the resident time decreased, it allowed less time for the pollutants to be absorbed by the photocatalytic compound.

The second phase was to evaluate the environmental effectiveness of TiO₂ photocatalytic pavements in photodegrading mixed NO₂ and NO gases from the atmosphere. The same four samples were used in phase two for further analysis of mix design factors. In addition, the known environmental factors of humidity level, and flow rate were also tested under various NO₂/NO_x ratios to identify any variable interactions. A partial factorial design was conducted for NO₂/NO_x, flow rate, aggregate structure, and TiO₂ content to provide an indication of the influence of each factor on the photocatalytic effectiveness. Based on the results of the experimental program, it is determined that the NO₂/NO_x ratio has a significant impact on NO_x reduction efficiencies; however, the extent of this impact relies on many other factors, such as flow rate.

Further investigation was conducted on identified significant variables, including the relative humidity, flow, mix design and NO₂/NO_x ratios to develop the associated trends and interactions. More humidity points were analyzed than phase one, which identified a optimum

relative humidity at 25%. Meanwhile, similar to phase one results, increasing the flow rate negatively affects the effectiveness of the NO_x reduction efficiency regardless of the NO₂/NO_x ratio. However, there is an interaction between the flow rate and the NO₂/NO_x ratio. This is a result of a possible reaction with the NO₂ and the concrete surface. At slow flows, most of the NO₂ is scrubbed through reaction, thus there is less of a negative impact on the NO_x reduction efficiencies. Further research should be conducted to confirm that this reaction, possibly heterogeneous hydrolysis, occurs at the concrete surface. Within the evaluated range, the titanium content and aggregate gradation had little impact on NO_x removal efficiency, supporting the results of phase one. Thus the optimum mix design would be 3% TiO₂, with normal aggregate gradation due to costs.

The third and final phase was to evaluate the environmental effectiveness of photocatalytic concrete surface layers in photodegrading NO_x, when exposed to common roadway contaminants. Three common roadway contaminants were chosen: dirt, de-icing salt, and motor oil. Each of these tested at two soilure coverage levels. A control test was also conducted which was tested with no soiling for comparison. The optimum mix design, determined from the previous two phases, was the photocatalytic pavement samples as used. Main effects of the relative humidity, contaminant coverage level, and flow rate were calculated for two levels for each factor; interactions between variables were identified. Further analysis was conducted on the significant variables identified, including contaminant, relative humidity, and flow to develop the associated trends.

The three contaminant types all had a strong negative impact on the photocatalytic NO_x removal efficiency. The impact of contaminant coverage was largely dependent on the soilure type, with oil having the largest negative impact. The mechanism for the negative impact is most

likely caused by competition for the adsorption areas. In addition, oil also competes with photocatalytic reactive sites and the larger negative impact could be a result of the photocatalytic degradation of oil, rather than the NO_x . An increase in the flow rate resulted in lower NO_x efficiencies. The increase in flow rates with the presence of contaminants at the surface resulted in a decrease in NO_x reduction efficiency. Although all soilure types exhibited similar decreasing trends with flow, salt decreased the most. However, complete photocatalytic ability was recovered after being rinsed with water. An increase in the relative humidity had a negative impact on NO_x reduction efficiency. Dirt and salt showed the most interaction with the relative humidity. For the salt, this could be related to a reaction taking place between water and salt at the concrete surface in which the resulting product increases the competition for adsorption area. As for the dirt, this could be a result of the relative humidity absorption capability of the dirt.

In conclusion, photocatalytic pavements have the potential to reduce significant amounts of NO_x pollution from roadway microenvironments. However, results of this study illustrate that the significance of photocatalytic pavement reduction is very complex, depending on several environmental factors common to highway microenvironments. As a result, further research is necessary before widespread implementation. An environmental pollution model to better understand how photocatalytic pavements would operate under real world conditions, rather than a controlled lab environment would be indicated. Further, a full-scale study to validate the efficiency of this technology in the field should be considered.

6.1 Future Work

Although photocatalytic pavements are proven effective in the lab, widespread implementation requires the following investigations:

- What reduction efficiencies are realized in real world environments and how significant are they compared to the pollution problem?
- What locations would be optimal for photocatalytic pavements?
- How much pollutants actually come in contact with the pavement surface?
- What is the durability of the layer?
- What is the shear strength of the layer?
- What is the impact of mixed gas environments?
- Are other pollutants reduced?
- Did the proposed photocatalytic layer mix design impact the surface friction?
- How much nitrates are released and will they contribute to eutrophication?
- Are any nanoparticles released to the environment, potentially posing an unintentional negative impact?
- What is the overall environmental impact?

In order to better understand the significance NO_x reduction potentially realized in the field, a chemodynamic model needs to be developed. Presently, kinetic models have been used to describe the reaction rates for photocatalytic materials. However, experimental data is needed for the proposed photocatalytic pavement to generate the relevant mass transport parameters to describe the NO_x absorption and NO_x photocatalytic reaction used in these kinetic models. Development of this model would be key for identifying key locations that would benefit most from photocatalytic pavements.

To verify the potential of photocatalytic pavements a field study needs to be completed. A field study would be identify how much pollutants come in contact with the pavement surface, evaluate the photocatalytic and pavement durability, identify any increase in nitrates in

stormwater runoff, and identify the potential of nanoparticle exposure. This data would be useful in assessing proposed chemodynamic models for photocatalytic pavements and identifying the validity of the lab experiments results in assessing photocatalytic pavements. Furthermore the results are necessary for a comprehensive life cycle assessment on photocatalytic pavements to measure its environmental impact. In addition to these results, reduction of pollutants other than NO_x should also be investigated.

Lastly, can photocatalytic pavements be used with other materials such as asphalt pavements or porous concrete?

APPENDIX

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Title: Laboratory Investigation of the Effect of Mixed Nitrogen Dioxide (NO₂) and Nitrogen Oxide (NO) Gases on Titanium Dioxide Photocatalytic Efficiency in Concrete Pavements

Author: Heather Dylla, Marwa M. Hassan, Marion Schmitt, Tyson Rupnow, et al.

Publication: Journal of Materials in Civil Engineering

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VITA

Heather Dylla was born in 1984 in Shakopee, Minnesota. In 2006, she finished her Bachelor of Science in Civil Engineering from Bradley University. Heather worked two years for Black and Veatch in the Project Controls on a design build for coal power plant projects. She joined Louisiana State University in August 2008 to pursue a Master of Science in Engineering Science degree. Her interests include sustainable engineering.